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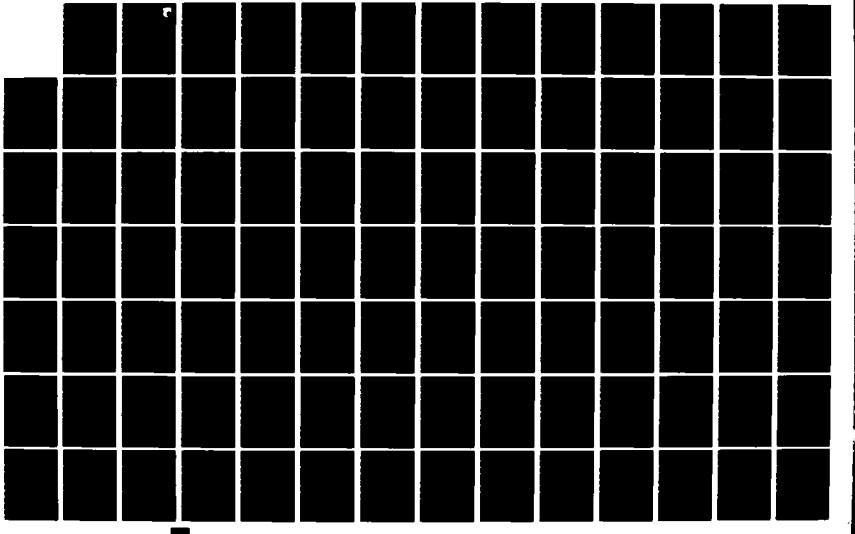

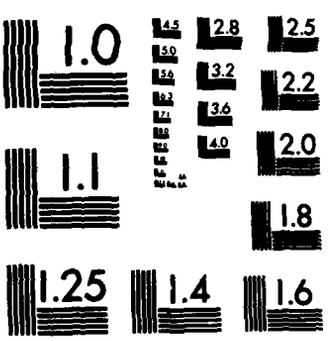

AFWAL-TR-83-4063

CHEMISTRY, CHARACTERIZATION AND PROCESSING OF IMC CURING POLYMERS

KREISLER S.Y. LAU

TECHNOLOGY SUPPORT DIVISION
HUGHES AIRCRAFT COMPANY
EL SEGUNDO, CA 90245

July 1983

Final Report for Period September 1979 to June 1983

Approved for public release, distribution unlimited

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FOR THE COMMANDER

Franklin D. Cherry, Chief
Nonmetallic Materials Division

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFWAL-TR-83-4063	2. GOVT ACCESSION NO. A133479	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* Chemistry, Characterization and Processing of IMC Curing Polymers		5. TYPE OF REPORT & PERIOD COVERED FINAL REPORT SEPTEMBER 1979 - JUNE 83 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Kreisler S. Y. Lau		8. CONTRACT OR GRANT NUMBER(s) F33615-79-C-5101
9. PERFORMING ORGANIZATION NAME AND ADDRESS Technology Support Division Hughes Aircraft Company El Segundo, CA 90245		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS PE 2419; Project 141904; Work Unit 24190419
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Material Laboratory (MLBC) Air Force Wright Aeronautical Laboratories Wright-Patterson AFB, OH 45433		12. REPORT DATE July 1983 13. NUMBER OF PAGES 140
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

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17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

intramolecular cycloaddition
solid state cure
polyimide
polyisomides
2,2'-bis(phenylethynyl)-5,5'-diaminobiphenyl
2,2'-bis(phenylethynyl)-4,4',5,5'-tetraaminobiphenyl

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

A variety of methods for a low-cost synthesis of the IMC curable monomer, 2,2'-bis(phenylethynyl)-4,4',5,5'-tetraaminobiphenyl, was explored without success. A low-cost route was found for the preparation of the IMC curable monomer, 2,2'-bis(phenylethynyl)-5,5'-diaminobiphenyl. Numerous model compounds with potential IMC reactions were prepared and characterized by thermal analysis. Some high molecular weight isoimide polymers were synthesized for study of the thermal rearrangement of the isoimide group to an imide group as an IMC-type reaction.

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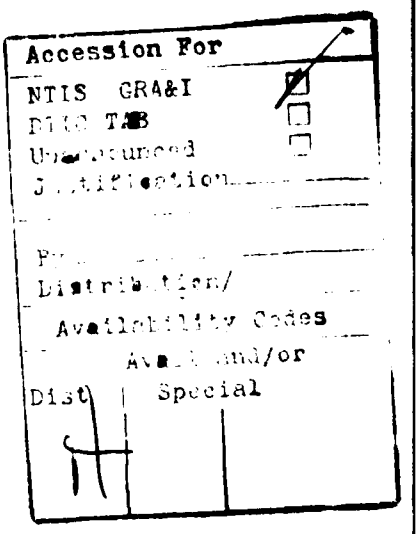
FOREWORD

This final report was prepared by the Materials Technology Department in the Technology Support Division of Hughes Aircraft Company, El Segundo, California 90245, under Air Force Contract F33615-79-C-5101, Program Element 2419, Project 141904, Work Unit 24190419, "Chemistry, Characterization and Processing of IMC Curing Polymers". The program was sponsored by the Air Force Wright Aeronautical Laboratory, Polymer Branch, with Dr. Frederick L. Hedberg as the Project Monitor.

Hughes Aircraft Company personnel who have contributed to the program include Dr. Kreisler S. Y. Lau (Program Manager and Principal Investigator), Dr. Richard I. Akawie, Mr. William B. Austin, Mrs. Danute I. Basiulis, Mr. T. Kirk Dougherty, Mr. William J. Kelleghan and Dr. Richard N. Leyden. In addition, Dr. Norman Bilow, Dr. Thomas W. Giants, Dr. Abraham L. Landis and Dr. Arthur B. Naselow served as internal consultants. Analytical chemistry support services and consultations in DSC-TGA analyses, FTIR spectroscopy, NMR spectrometry, vapor-phase osmometry, and HPLC-GPC analyses were provided by the analytical chemistry groups headed by Mr. Philip G. Magallanes and Mr. Herman S. Noji.

This report covers work performed during the period of September 17, 1979 through June 23, 1983.



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SECTION I

INTRODUCTION

Significant progress has been made in recent years in the synthesis and development of new polymer materials, particularly organic polymers, which have specific qualities to satisfy certain existing criteria of high performance in extreme service conditions. Some of the properties which characterize high performance are high rigidity, high tensile strength, thermo-oxidative stability and resistance against swelling, dissolution and chemical deterioration (Reference 1). The low-density (light weight) characteristic of the high performance organic polymers compares favorably with metallic materials, especially when reduction in weight is essential to improvement in high-speed weapon systems and aircraft and spacecraft construction.

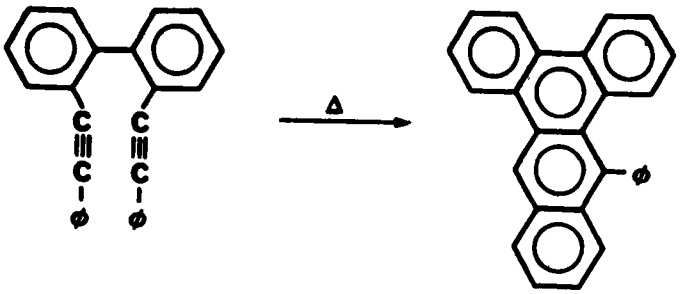
Structure-property relationships developed over the years show that the incorporation of aromatic nuclei in the polymer imparts thermal stability to the system. The presence of aromatic-heterocyclic rings also contributes to the adhesive and cohesive qualities of the polymer (Reference 2). Examples are found in the application of high-modulus, high-strength aromatic polyamide fibers as reinforcing agents in elastomeric systems, such as radial tires, and in hard and strong resins, such as those used for the construction of parts in spacecraft, airplanes, automobiles and buildings. Polyimides, polybenzimidazoles, polyoxadiazoles and polyquinoxalines are important not only in film and membrane technology, but also in applications such as glass- and graphite-reinforced composites, molding compounds, solid composite lubricants, thermally resistant coatings, and adhesives for titanium, steel, ceramics and composites.

One approach to structural modification of high temperature polymers to improve processibility is to utilize reactive oligomers which have good solubility-fusibility and flow properties. Heterocyclic oligomers, namely the quinoxaline ATQ oligomers (Reference 3) and imide oligomers (References 4, 5) containing terminal acetylene groups, can homopolymerize by both inter- and intramolecular addition reactions to fused aromatic ring systems which are thermo-oxidatively stable. The thermally-induced acetylene reaction during cure affords resins that have excellent thermal stability. Most importantly, no evolution of volatiles occurs during cure. Studies directed to resolving the mechanistic aspects of the cure reaction were undertaken (References 4, 6, 7, 8, 9).

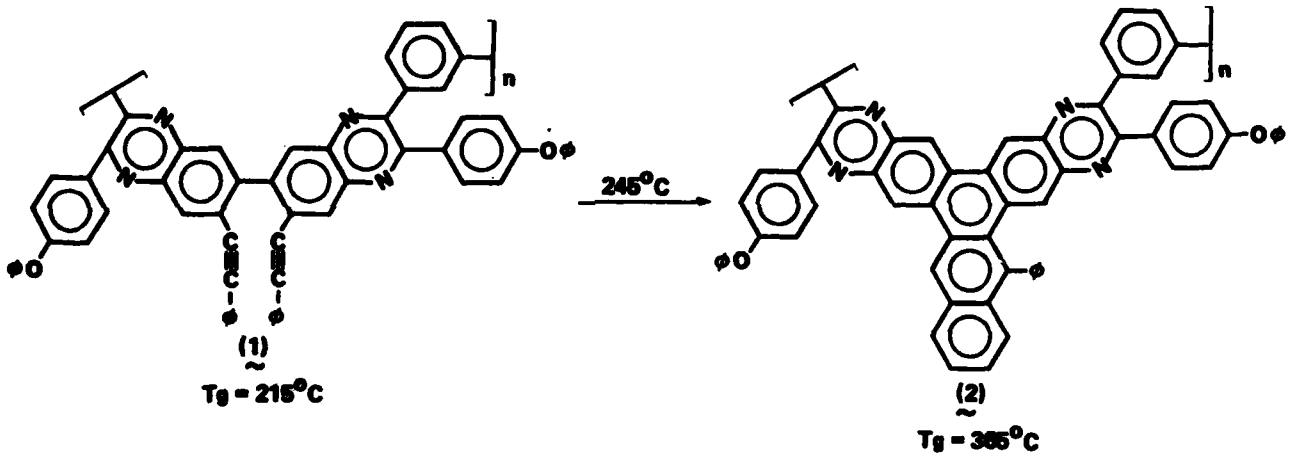
Processing of a thermoplastic material (e.g., polyphenylquinoxaline resin) as a fiber-reinforced composite requires high temperature in both consolidation and thermoforming so that adequate flow and wetting of the fibers can be achieved. The introduction of a structurally compatible plasticizer aims at the reduction of the required high temperatures for fabrication. The ideal plasticizer must lower the effective softening point of the thermoplastic resin during processing and then undergo polymerization or inter- and intramolecular reactions without the generation of volatiles to produce a high temperature resistant network or filler structure imbedded in the thermoplastic (Reference 10).

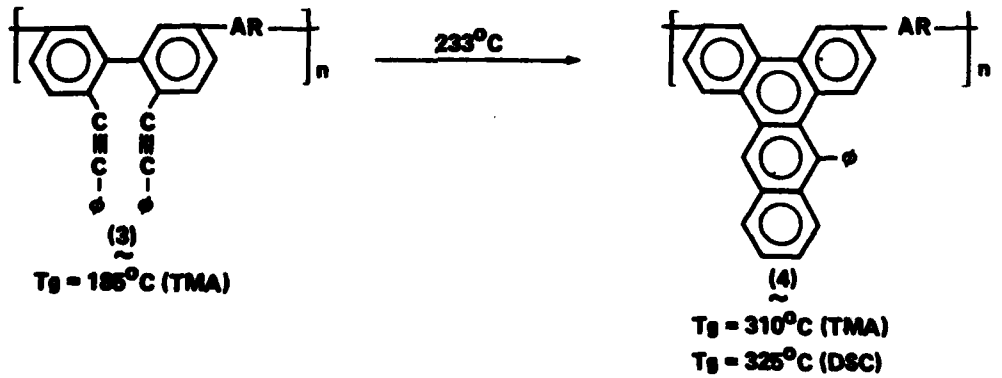
In general, thermoplastics having a softening temperature around 200°C or below can have easier flow and processibility. However, it is obvious that the resultant composites will soften and lose their mechanical strength at temperatures approaching the softening point. In order to raise the softening point of the polymer after fabrication, a thermal curing process is required to bring about intermolecular crosslinking. Employing a certain percentage of a trifunctional monomer in the polymer synthesis will afford pre-disposed crosslinking sites along the polymer backbone. Complications often arise in branching and gelation during synthesis or storage of prepolymer solutions (Reference 2). Other crosslinking methods, e.g., free radical formation and recombination along the polymer backbone by radiation or free-radical initiation and chemical reaction of incorporated pendent groups, often result in the evolution of volatiles, creating voids in the composite structure. The three-dimensional network formed after crosslinking causes brittleness in the structure. Furthermore, the softening temperature of the polymer can be raised only as high as the temperature used for the curing process. The cure temperature thus dictates the ultimate use temperature for the composite structure.

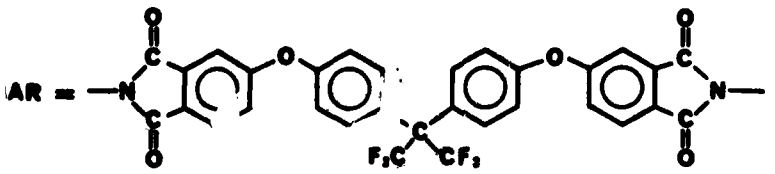
The development of the intramolecular cyclization (IMC) cure method effectively eliminates the restriction of translational molecular mobility needed for crosslinking cure. Thus, the thermal cure step, which causes pairs of strategically positioned pendent groups along the polymer chain to undergo an intramolecular cycloaddition to form a fused aromatic structure, can continue to completion long after the resin is essentially vitrified. The ultimate use temperature would be substantially higher than the cure temperature. The intramolecular nature of the curing process precludes the formation of a three-dimensional structure. Since the reaction used for the curing process is of the cycloaddition type, no volatiles are evolved. The thermal cycloaddition reaction of 2,2'-bis(phenylethynyl)biphenyl (References 11, 12) has been successfully adopted for the IMC cure studies.



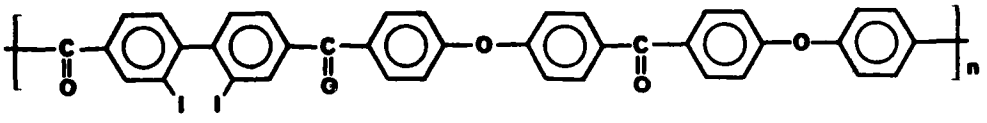
In the case of the prepolymer polyphenoxyphenylquinoxaline (PPQ) 1, a 120°C advancement in Tg could be obtained in the cured polymer 2 after an overnight cure at 245°C (References 13, 14). The polyimide prepolymer 3 containing the hexafluoroisopropylidene group has the lowest Tg of all the polyimides studied (References 15, 16). Thermal curing studies of 3 again showed a substantial enhancement in the Tg value with the formation of the cured polymer 4.





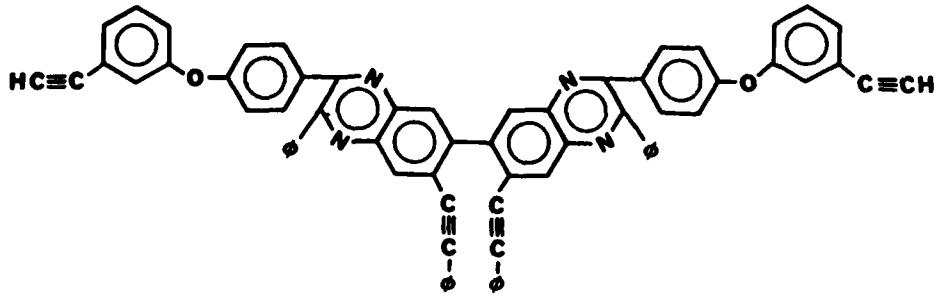


An alternative approach to incorporate the 2,2′-bis(phenylethynyl)biphenyl units into the polymer backbone of polyaromatic ether-keto-sulfones appeared to be unsatisfactory (Reference 17). Treatment of the preformed polymer 5 with copper[I] phenylacetylide afforded a product with a poor analysis for the bis(phenylethynyl) derivative. The incomplete reaction was probably the result of inhomogeneity in the phenylethynylation reaction medium. Attempts were made to improve phenylethynylation of these polymers (References 18, 19, 20, 21).



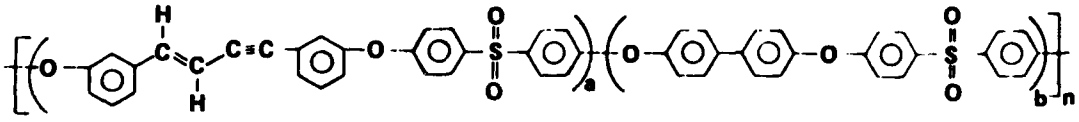
(5)

High molecular weight thermoplastic polymers including the IMC polymer 3 suffer from inadequate flow during fabrication prior to cure. Recent AFWAL research effort (work done at the Polymer Branch) directed toward solving the flow problem has culminated in the development of an acetylene-terminated quinoxaline 6, which exhibited a low melt-flow temperature of 107°C and an exotherm above 150°C corresponding to crosslinking reaction at the terminal acetylene groups and intramolecular cyclization reaction of the phenylethynyl pendants (Reference 22). Adequate flow was achieved by virtue of the large "window" between the melting and curing temperatures.



(6)

It was postulated that a diaryl enyne unit when incorporated into a high molecular weight polymer would undergo a thermal intramolecular cyclization reaction to generate a new aromatic nucleus (Reference 23). Such a cyclization would raise the Tg of the polymer. The polysulfone 7 (a = 100%, b = 0%) and its copolymers (a = 10% to 50%, b = 50% to 90%) have been synthesized. Curing of 7 at 250°C yielded an insoluble, dark, very brittle material, indicating that interchain crosslinking, instead of the desirable intramolecular cyclization, had occurred.



(7)

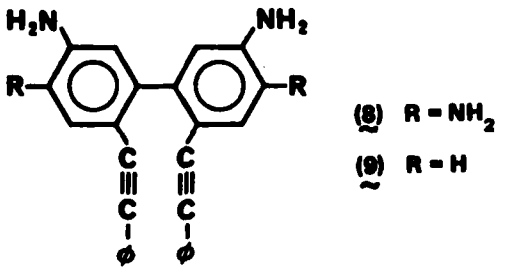
The concept of intramolecular cyclization (IMC) cure for the advancement of Tg has thus far been demonstrated only with the thermal conversion of 2,2'-bis(phenylethynyl)biphenyl to 9-phenyldibenz[a,c]anthracene. It would be advantageous and desirable to be able to extend the IMC concept to other chemical systems. Several structural requirements for the potential IMC systems are important. First, the expected IMC reaction must be thermally induced and should not liberate gaseous by-products. Second, the end product of the thermal IMC reaction should be a fused aromatic ring system and/or contain trivalent nitrogens for high thermo-oxidative stability. Third, terminal phenyl rings should be present to allow functionalization. Fourth, the structural unit that undergoes the IMC reaction should be as flexible as possible so that it may contribute to the lowering of the Tg of the pre-cure polymer, an important objective in the improvement of processibility.

SECTION II

RESULTS AND DISCUSSION

1. TASK I: SYSTEMATIC STUDIES IN MONOMER SYNTHESIS

The state-of-the-art IMC system is the thermal cyclization reaction of 2,2′-bis(phenylethynyl)biphenyl (References 11, 12) which has been successfully adopted in the studies of several quinoxaline (References 13, 14) and imide polymers (References 15, 16, 17). The synthesis of thermoplastic and thermosetting quinoxalines requires 2,2′-bis(phenylethynyl)-4,4′,5,5′-tetraaminobiphenyl (8) as the precursor, whereas the synthesis of imides requires 2,2′-bis(phenylethynyl)-5,5′-diaminobiphenyl (9).

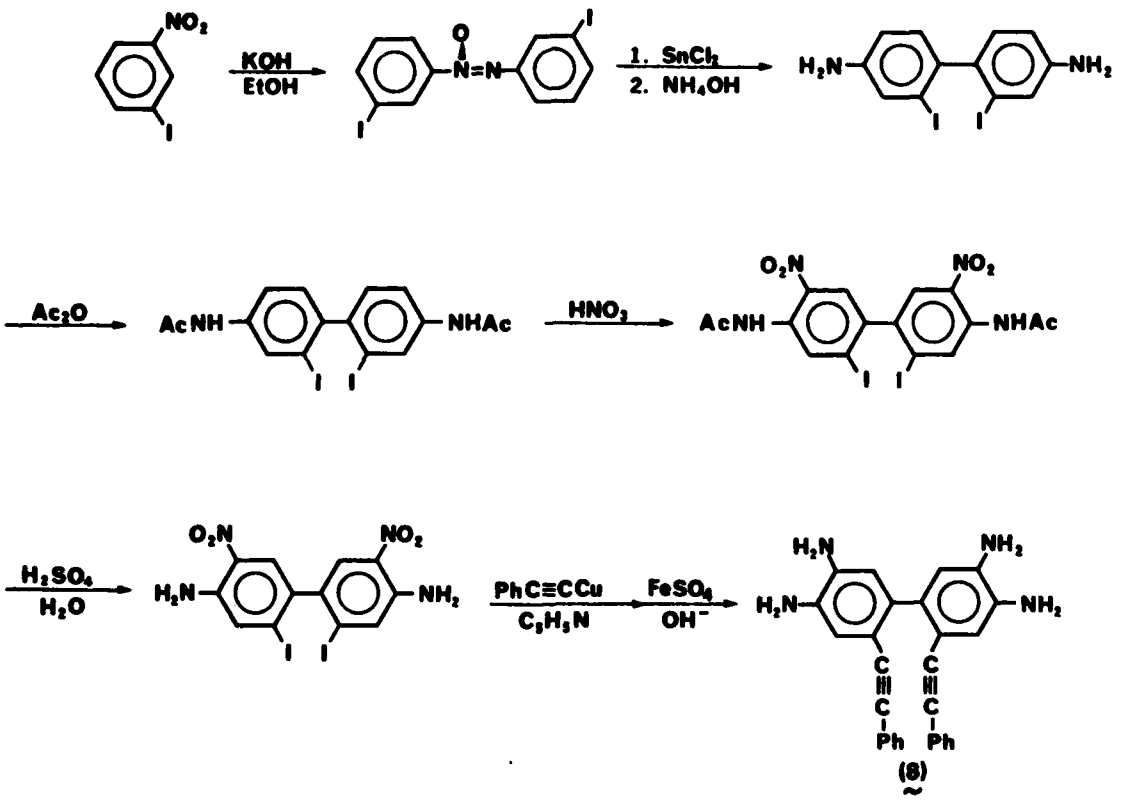


(8) R = NH_2

(9) R = H

Procedures for the synthesis of 8 and 9 have been successfully established at the AFWAL laboratories (References 2, 15, 17). Task I of the current research program was to develop low-cost alternative(s) for the synthesis of 8 in view of the fact that the AFWAL procedure (Scheme 1) is quite laborious and low of yield.

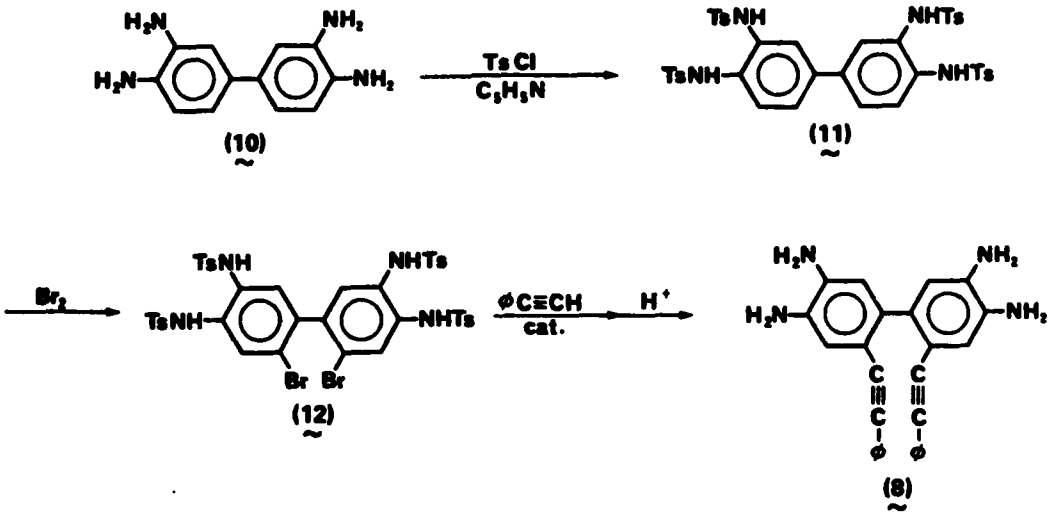
Scheme 1



Inasmuch as we recognize the significance of the key intermediate 8, we propose several alternative low-cost routes to its attainment. Factors under consideration are the yield of each step of the procedure, the low-cost availability of starting materials, and the ease of the overall operation.

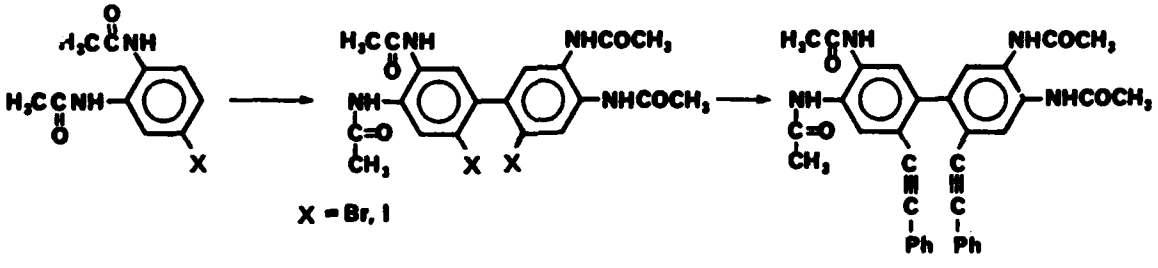
One method we originally proposed involves commercially available 3,3′-diaminobenzidine 10 (via the Upjohn method) which can be tosylated to yield the tetratosylamide 11. The tosylamido groups subsequently dictate regiospecific para-bromination (Reference 24) to give 12, which can be phenylethynylated by some organometallic procedure. Two organopalladium systems are generally available for the coupling between an aryl halide and phenylacetylene (References 25, 26, 27), both being superior to an earlier copper[I] phenylacetylide method (References 28, 29, 30) in terms of simpler operational procedure and higher yields. The application of the organopalladium methods to 12 and other similar 2,2′-dihalo biphenyls was found to be complicated by an anomalous reaction (vide infra). The copper[I] phenylacetylide method should be used. Subsequent removal of the tosyl groups from the phenylethynylated product generates the desired compound 8 (Scheme 2). This approach was studied by an in-house effort at the AFWAL Polymer Branch.

Scheme 2

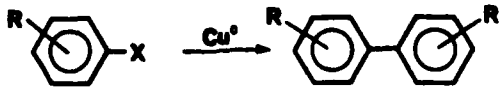


Biaryl Coupling Reactions

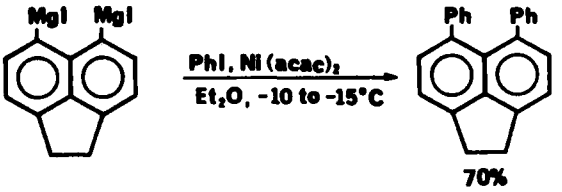
We consider the biaryl coupling reaction the most efficient approach to the synthesis of 8, as long as the aryl compound can be easily constructed.



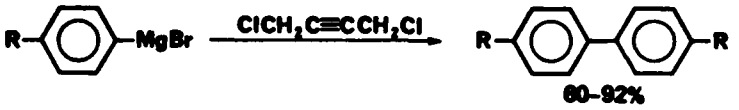
Biaryl formation through the coupling of aryl halides in the presence of copper metal, i.e., the Ullmann reaction (References 31, 32, 33, 34), generally requires high temperatures. Moderation of the reaction temperatures can be brought about by special preparations of activated copper (References 35, 36, 37, 38). Alternatively, copper[I] t-butoxide has been found to effect Ullmann-type biaryl coupling (Reference 39).



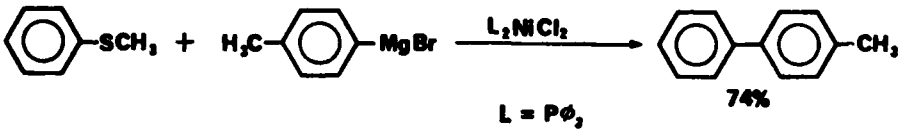
Preformed organometallic intermediates, for example, arylmagnesium halides (References 40–46) or aryllithium reagents (References 47, 48) can be converted to biaryls in the presence of any of a variety of metallic reagents or an organic promotor such as 1,4-dichloro-2-butyne (Reference 46). Recently, the reactions of aryl sulfides with arylmagnesium bromides, mediated by the catalytic action of dichlorobis(triphenylphosphine)nickel[II], have been shown to yield biaryls (Reference 49).



(Reference 45)

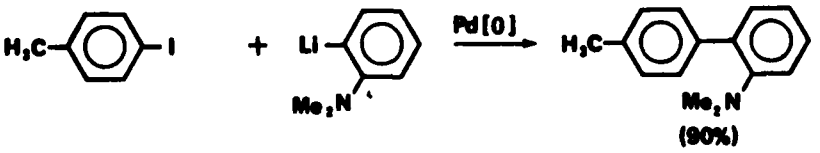


(Reference 46)

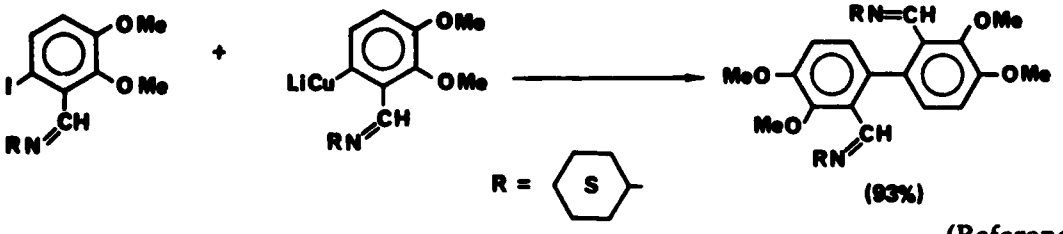


(Reference 49)

The palladium[0]-catalyzed arylation of 4-iodotoluene with 2-(dimethylamino)phenyllithium gives the biaryl product in 90% yield (Reference 50). In a key step in the synthesis of juncusol, the substituted biaryl compound was prepared via the coupling reaction of the cuprate intermediate with the appropriate aryl iodide (Reference 51).



(Reference 50)



(Reference 51)

Arylboranes give good yields of biaryls in the presence of alkaline silver nitrate (Reference 52). As the arylboranes are prepared from aryl halides, magnesium and diborane, functional groups that are sensitive to the Grignard conditions cannot be tolerated.

$$2\ ArX \xrightarrow[BH_3/THF]{Mg} \xrightarrow[MeOH,\ KOH]{AgNO_3} Ar\text{-}Ar \qquad \text{(Reference 52)}$$

Zero-valent organonickel complexes react stoichiometrically with aryl halides providing a novel entry in the synthesis of biaryls (References 53, 54). The yields are generally high and sensitive functional groups such as ketone, aldehyde, ester and nitrile survive the mild reaction conditions. However, ortho substituents, nitro groups and acidic functional groups inhibit the coupling reaction, and zero-valent nickel complexes require special manipulation under inert atmosphere in a dry box.

$$2\ ArX + Ni(COD)_2 \xrightarrow[DMF,\ 25\text{-}40°C]{} Ar\text{-}Ar + NiX_2 + 2\ COD$$

In situ generation of a solvated zero-valent nickel reagent from dichlorobis(triphenylphosphine)nickel[II] was effected with zinc in the presence of triphenylphosphine. Tris(triphenylphosphine)nickel[0] thus formed causes biaryl coupling of aryl halides in good-to-excellent yields (Reference 55).

$$2\ ArX \xrightarrow[DMF,\ 50°C]{Ni(PPh_3)_3} Ar\text{-}Ar + NiX_2 + 3\ PPh_3$$

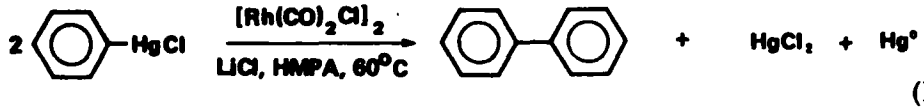
An alternative in situ generation of nickel[0] was carried out electrochemically at 60°C in a divided cell containing dichlorobis(triphenylphosphine)nickel[II], triphenylphosphine and tetra-n-butylammonium bromide in dimethylformamide with a lead plate as cathode and a platinum plate as anode (Reference 56). Catalytically, nickel[0] effects biaryl formation from aryl halides (Br, I) in the presence of excess zinc powder. The presence of triphenylphosphine ligands is not absolutely required (References 57, 58).

Palladium on charcoal has also been shown to catalyze biaryl formation from aryl halides in the presence of selected surfactants, e.g., cetyltrimethylammonium bromide, in an aqueous alkaline sodium formate medium (Reference 59).

$$2\ ArX \xrightarrow[H_2O\text{-}NaOH\text{-}HCOONa,\ 95°C]{surfactant,\ Pd\text{-}C} Ar\text{-}Ar$$

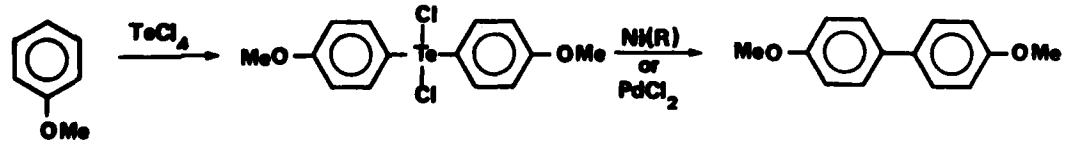
The significance of arylmercurials in organic synthesis has recently been enhanced by the ease with which these compounds are obtained through direct electrophilic aromatic mercurtion (Reference 59). Previously, the dimerization of diarylmercury and arylmercurials at elevated temperatures in the presence or absence of palladium salts and other transition metals was found to give low yields of biaryls (References 60, 61, 62, 63, 64, 65). More recent developments showed that arylmercurials can be converted to biaryls in good yield and under mild conditions by treatment with copper metal and a catalytic amount of palladium chloride in pyridine (Reference 66). Amine and amide functions are compatible with the reaction conditions but phenols and carboxylic acids fail to react. The best organomercury method (based on simplicity in operation and mild conditions) appears to be the rhodium[I]-catalyzed dimerization of arylmercurials (Reference 67).

$$2\ ArHgX + Cu^{\circ} \xrightarrow[C_5H_5N,\ 115^{\circ}C]{PdCl_2} Ar\text{-}Ar + 2\ Hg^{\circ} + CuX_2$$ (Reference 66)



(Reference 67)

All the above methods for biaryl formation require halogen-substituted aromatics as starting materials and the halogens are eventually lost. A direct and regiospecific coupling of the aromatics is of great interest. Bis(aryl)tellurium dichlorides are readily available and can be converted with degassed Raney nickel to give the corresponding biaryls (Reference 68). In lieu of Raney nickel, which must be prepared by a tedious procedure, palladium[II] dichloride was later used to arrive at the same end results (Reference 69).

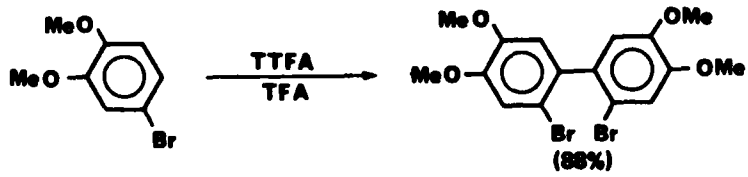


Thallium[III] trifluoroacetate in trifluoroacetic acid was found to be extremely efficient in promoting direct oxidative coupling of a variety of substituted aryl halides to symmetrical biaryls (Reference 70). In the past decade, most of the work on organothallium chemistry has been carried out by McKillop and Taylor and coworkers, who are primarily responsible for the application of various thallium[III] reagents in organic synthesis (References 71, 72, 73, 74). In particular, enhancement of the electrophilic properties of thallium[III] trifluoroacetate (TTFA) relative to thallium[III] acetate, together with its ease of synthesis, makes it a

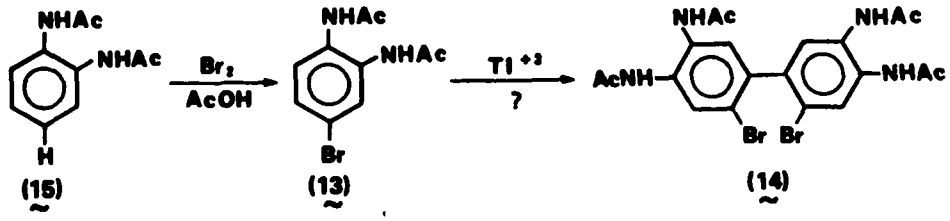
convenient reactive thallation reagent. The products of thallation, arylthallium bis(trifluoroacetates), undergo a variety of substitution reactions yielding, for example, aryl iodides (References 75, 76), aryl fluorides (Reference 77), aryl nitriles (Reference 78), thiophenols (Reference 71), and phenols (Reference 78).

The reactivity of TTFA as an oxidizing agent was exemplified by the conversion of phenols into para-quinones (References 79, 80). Oxidative non-phenolic coupling of aromatic compounds promoted by TTFA also provides a valuable access to natural products otherwise difficult to synthesize (References 81, 82). The facile oxidative coupling of aryl halides by TTFA to give symmetrical biaryls (Reference 70) presumably takes place via a radical cation mechanism (Reference 83). Both oxygen and halogen functions on the aromatic substrates can be tolerated.

The high-yield conversion of 4-bromoveratrole to 2,2′-dibromo-4,4′,5,5′-tetramethoxybiphenyl by TTFA prompted us to investigate, as our initial direction in Task I, the thallium route for the conversion of 1,2-diacetamido-4-bromobenzene (13) to 2,2′-dibromo-4,4′,5,5′-tetraacetamidobiphenyl (14) which is the logical precursor to our target compound, 8.



(Reference 70)



Organothallium Chemistry of Aromatic Amides: Oxidative Intramolecular Cyclization

Compound 15 was synthesized and characterized (References 84, 85). Bromination of 15 was effected in acetic acid at 10–15°C. The product contained ca. 9% of dibromo material as determined by mass spectrometry and elemental analysis. This result was similarly observed at AFWAL. The monobromo derivative 13 was purified by repetitive recrystallizations. Although it has an attractive analogy in the reported conversion of 4-bromoveratrole to 2,2′-dibromo-4,4′,5,5′-tetramethoxybiphenyl (Reference 70), the organothallium chemistry of aromatic amides is not known. Instead of biaryl coupling, compound 13 underwent mono nuclear oxidation in the presence of TTFA to yield 4-acetamido-6-bromo-2-methylbenzoxazole (16, 24%) and 2-acetamido-5-bromo-1,4-benzoquinone (17, 3%) (Reference 86).

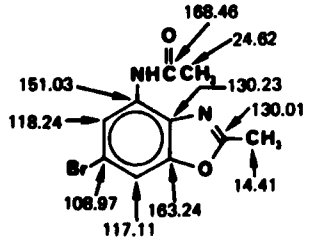
In a typical reaction, TTFA (7.5 mmoles) was weighed out under argon and dissolved in 35 ml of trifluoroacetic acid. The solution was then quickly added to 15 mmoles of 13 under argon. The red-brown reaction mixture was stirred and heated at reflux (73°C) for 2 hours in the dark. After aqueous workup and solvent removal, the solid residue was extracted with ether to separate the soluble products from the insoluble, unreacted starting material. The impure solid mass obtained from the ethereal solution was then purified by silica gel column chromatography to give first pure 17 in the chloroform eluate and then pure 16 in the 1 : 1 chloroform-ether eluate. No reaction occurred when the reactant mixture was stirred for 2 hours at 20–25°C. Extension of the reflux period to 24 hours did not increase the yield of products. When double the theoretical amount of TTFA was used, the yields were not increased, but there was a larger amount of highly colored impurities. Washing the chloroform extracts with saturated aqueous sodium bicarbonate was absolutely necessary, for no pure product was isolated when this washing was omitted.

Structure elucidation for compound 16 (white crystalline solid, mp 160.5–162°C) and compound 17 (lustrous golden platelets, mp 186°C) was accomplished by IR, MS, NMR and elemental analysis.

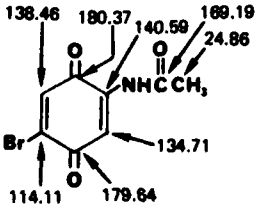
The poor material balance (>70% of the organics could not be retrieved from the aqueous solution even after repetitive extractions with chloroform) was probably due to strong complexation of the acetamido groups with TTFA. Tosylation (instead of acetylation) of the amine functions on 4-bromo-1,2-diaminobenzene was expected to suppress the complexation with thallium on both steric and electronic grounds. Consequently, 1,2-bis(4-tolylsulfonamido)-4-bromobenzene was synthesized and allowed to react with TTFA.

The crystalline product (mp 215–216°C) gave a positive Beilstein test and was identified as 7-bromo-2-(4-tolyl)-4-(4-tolyl)sulfonamido-1,2,3-benzoxathiazole 2-oxide (18) (70% yield) by IR, MS, NMR and elemental analysis.

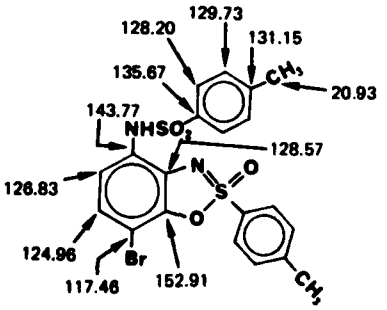
Carbon-13 NMR spectral characteristics for compounds 16, 17 and 18 are consistent with the assigned structures. The chemical shift values are downfield from TMS internal standard. The solvent used for 16 and 17 was deuteriochloroform, and for 18, DMSO-d_6. These results are first examples of an oxidative intramolecular cyclization pathway (Reference 87) of aromatic amides in the presence of TTFA.



(16)



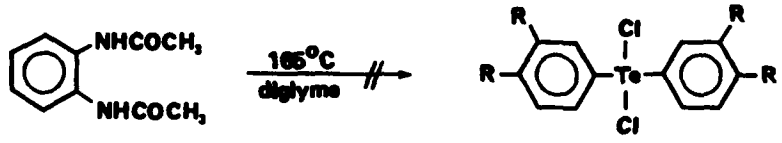
(17)



(18)

The Organotellurium Approach

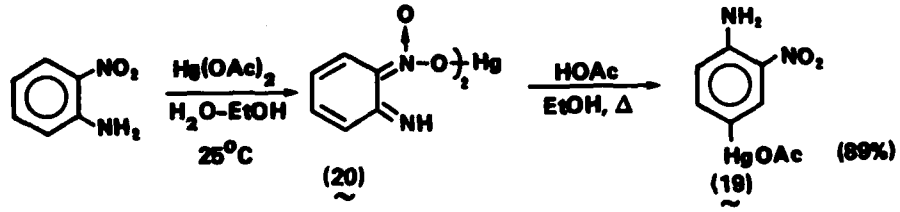
An alternative approach utilizing organotellurium reagents (References 68, 69) was briefly examined. Thus, 1,2-diacetamidobenzene was allowed to react with tellurium [IV] chloride in deaerated diglyme at 165°C. The product isolated at the end of the experiment gave an infrared spectrum that was devoid of the carbonyl absorption, suggesting decarbonylation of the acetamido groups in the starting material. This product was not characterized.



R = $NHCOCH_3$

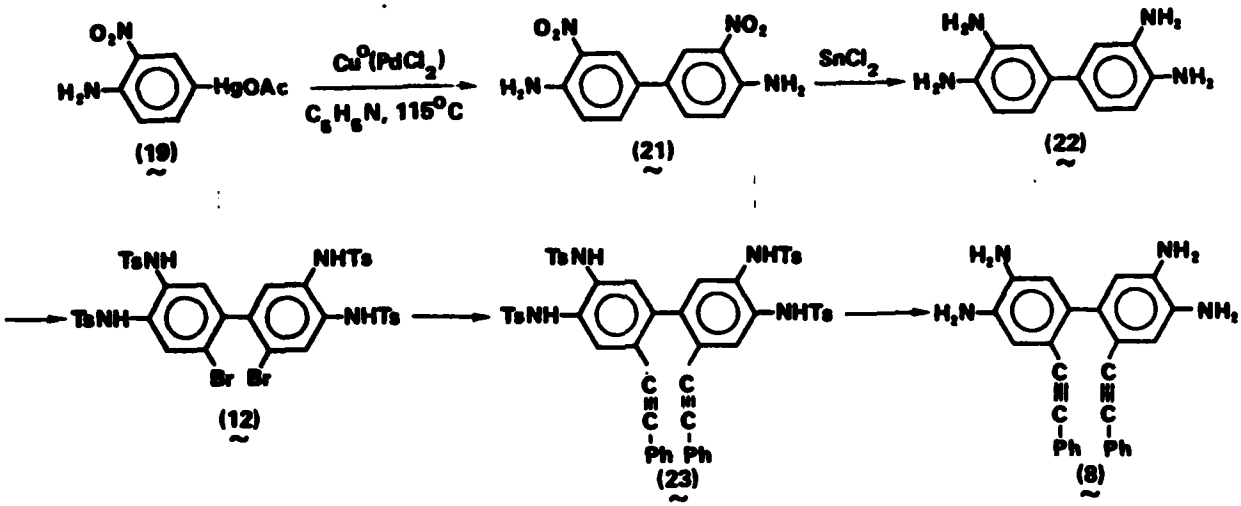
The Organomercury Approach

Mercuration of 2-nitroaniline with mercury[II] acetate afforded bright yellow 3-nitro-4-aminophenylmercury[II] acetate (19) in excellent yields. The transformation can be carried out in one pot, although the intermediate bright orange-red oxy complex 20 is isolable with ease (References 88, 89).



The aryl mercurial 19 was converted to 3,3′-dinitro-4,4′-diaminobiphenyl (21) by treatment with copper metal and a catalytic amount of palladium[II] chloride in pyridine (Reference 65). A chemical reduction of 21 gave 3,3′-diaminobenzidine, DAB, (22). Concurrent AFWAL effort established the feasibility of tetratoluenesulfonation of 22 and the subsequent bromination to give 12 (Scheme 3) which led eventually to 23 and 8.

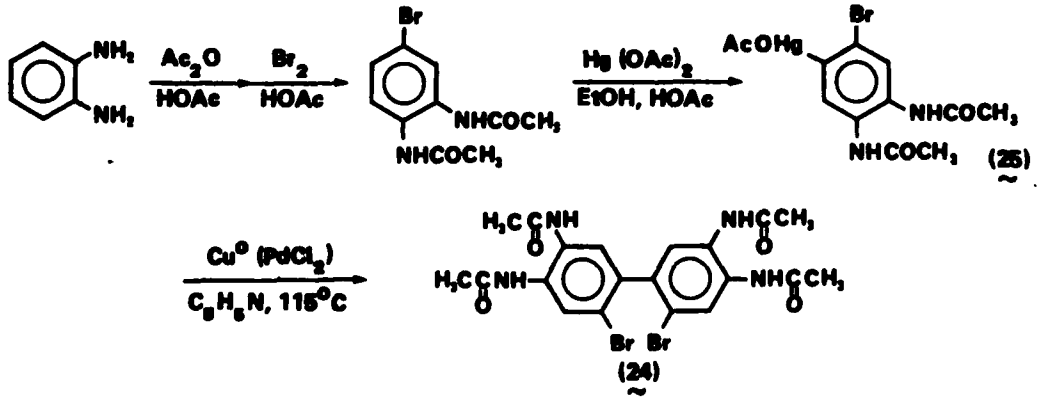
Scheme 3



Our synthesis of DAB (22) requires inexpensive starting materials. The operational steps are quite simple and will not present tedious manipulation in scale-up processes. The isomeric purity of the end product is expected to be high. The latter criterion is of utmost importance in the synthesis of high molecular weight polymers. Commercial DAB is expensive in small quantities. From a European source, the DAB is not isomerically pure. Alternatively, DAB can be obtained from an aminolysis procedure applied to the highly carcinogenic precursor 3,3'-dichlorobenzidine, produced by the Upjohn Company (Michigan).

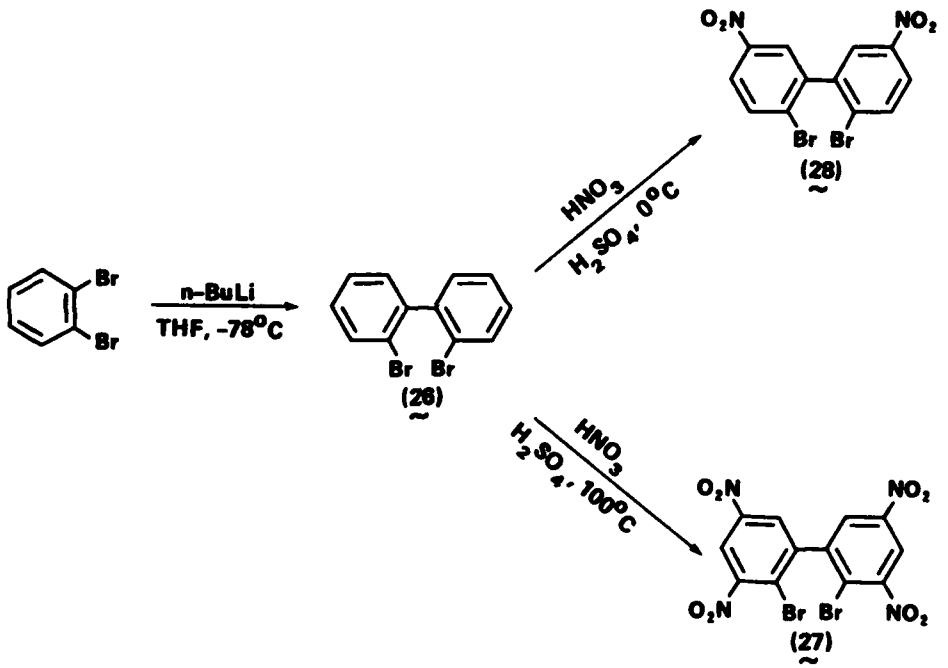
An alternate approach to the synthesis of an analog (24) of 23 is conceivable (Scheme 4). The steps leading to the mercurial 25 have literature precedents as high-yield reactions. Furthermore the starting material, o-phenylenediamine, is inexpensive and these steps can be effectively combined into a single operation. This approach has been the subject of an AFWAL in-house project.

Scheme 4



The Organolithium Approach

Still another biaryl coupling procedure seems applicable. Commercially available 1,2-dibromobenzene was converted to 2,2′-dibromobiphenyl (26) in high yields (Reference 90). Nitration of 26 at 100°C resulted in quantitative tetranitration but the product 27 does not have the desired 4,4′,5,5′-substitution pattern (Reference 91). The NMR coupling constant measured for the aromatic protons is consistent with a meta relationship. Treatment of compound 27 with two equivalents of phenylacetylene in the presence of palladium[II] acetate and triphenylphosphine did not effect replacement of the bromine atoms by the phenylethynyl groups. Virtually quantitative recovery of 27 was realized. The steric hindrance seems insurmountable for the replacement.



The tetranitration reaction takes place in two steps. Under milder conditions (<25°C), only dinitration occurs to yield the 5,5′-dinitro compound 28 (References 92, 93). The introduction of the nitro functions at the 4,4′- positions can be accomplished after prior reduction of the 5,5′- nitro groups in 28 and protection of the subsequent diamine. Such a procedure bears a resemblance to the original AFWAL synthesis of 8 (vide supra).

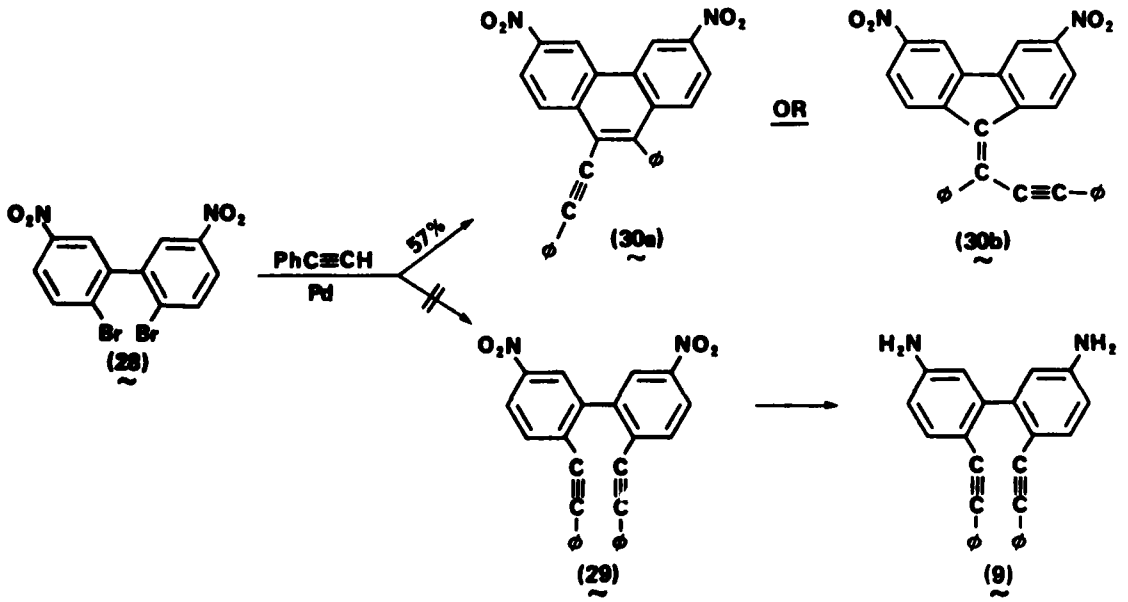
It is evident that 2,2′-dibromo-5,5′-dinitrobiphenyl (28) is a logical precursor to 2,2′-bis(phenylethynyl)-5,5′-diaminobiphenyl (9). Thus, a more efficient alternative synthesis of 9 is at hand to improve on the original AFWAL synthesis (Reference 15) which seems quite laborious.

Anomaly in Palladium-Catalyzed Phenylethynylation of 2,2′-Dihalobiphenyls

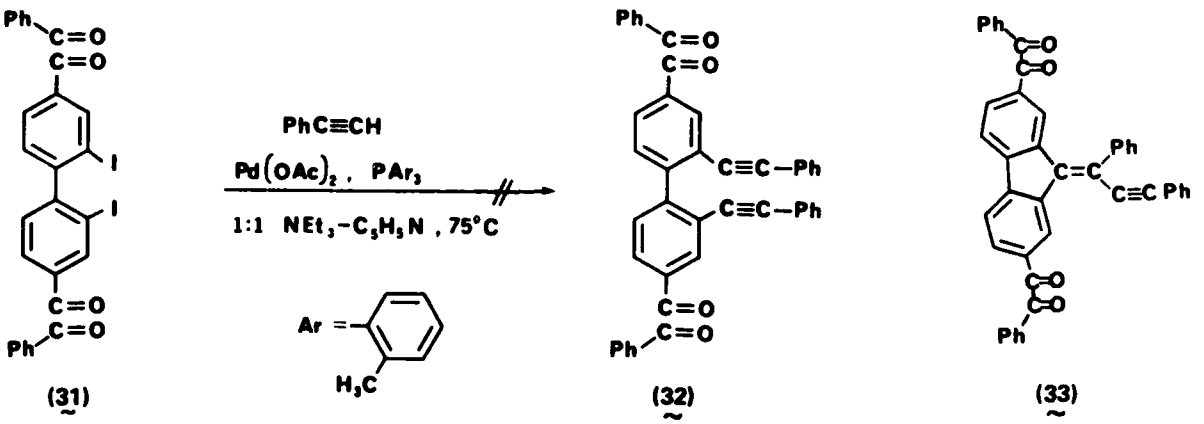
We succeeded in optimizing the reaction conditions so that crystalline 2,2′-dibromo-5,5′-dinitrobiphenyl (28) can be consistently isolated in better than 65% yield. The state-of-the-art phenylethynylation procedure is the palladium-catalyzed coupling reaction between an aryl halide (Br, I) and phenylacetylene.

The palladium-catalyzed coupling reaction (Reference 25) between an aryl halide and a terminal acetylene in the synthesis of aryl alkyl acetylenes (Reference 94), tolanes (References 95, 96) and heteroaryl acetylenes (References 97, 98) has received considerable attention in recent years. In similar synthesis of acetylenic compounds, the alternative organo-copper method (References 28, 29, 30, 99) is also widely accepted. These two approaches have been shown to be superior to many tedious classical methods (Reference 100).

The catalytic nature of palladium-promoted phenylethynylation of aryl halides is attractive. In principle, the presence of electron-withdrawing groups on the aryl halide facilitates the reaction (Reference 25). Treatment of a mixture of 28 and two equivalents of phenylacetylene in a 1 : 3 triethylamine-toluene solvent at 100°C in the presence of a $Ph_3P/(Ph_3P)_2PdCl_2/Cu_2I_2$ catalyst system (Reference 27) afforded a bright orange crystalline solid in 57% yield after chromatographic purification. This compound (mp >300°C) was not the expected 2,2′-bis(phenylethynyl)-5,5′-dinitrophenyl (29) (Reference 15). Infrared analysis showed a sharp C≡C absorption at 2175 cm^{-1} and two intense nitro absorptions at 1515 and 1340 cm^{-1}. Elemental analysis was consistent with $C_{28}H_{16}N_2O_4$ (Calculated: C, 75.67; H, 3.63; N, 6.30. Found: C, 75.59; H, 3.69; N, 6.24). The available data supported structure 30b. The alternative structure 30a was unambiguously ruled out by Carbon-13 and 250 MHz proton magnetic resonance studies (vide infra).

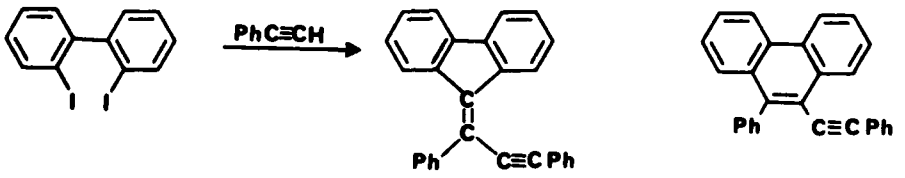


Under the catalysis of palladium acetate-tris(o-tolyl)phosphine (Reference 101) in 1 : 4 triethylamine-toluene solvent, 28 underwent phenylethynylation with two equivalents of phenylacetylene to yield the same product 30. In a comparative study at AFWAL, 4,4'-bis(phenylglyoxalyl)-2,2'-diiodobiphenyl (31) underwent phenylethynylation but did not yield the expected derivative 32 (Reference 102). The product is likely to have structure 33.



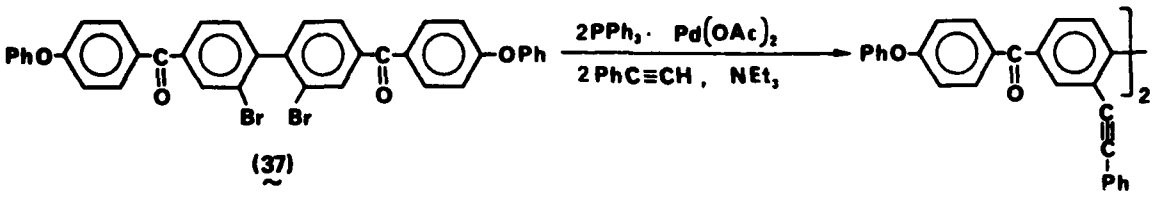
(31) (32) (33)

2,2'-Dibromobiphenyl (26) was allowed to react with phenylacetylene in the presence of palladium acetate-tris(o-tolyl)phosphine in 1 : 1 triethylamine-toluene for 24 hours at 90°C. The conversion was incomplete, as indicated by a 40% yield of triethylamine hydrobromide. In comparison, 2,2'-diiodobiphenyl (34) (Reference 11) underwent palladium-catalyzed phenylethynylation to give a 78% yield of a bright yellow crystalline compound (35) which was isomeric with 2,2'-bis(phenylethynyl)biphenyl (Reference 11), expected from a normal double phenylethynylation reaction.



(35b) (35a)

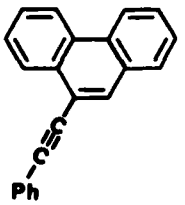
These results are in disagreement with the literature report (Reference 18) that the bis-phenylethynylated compound 36 was obtained in 44% yield from 37, using the palladium acetate-triphenylphosphine catalyst system.



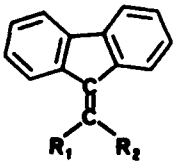
(37) (36)

Structure Elucidation Studies of Product from Anomalous Palladium-Catalyzed Phenylethynylation

Based on carbon-13 and 250-MHz proton magnetic resonance spectrometry, the products of the palladium-catalyzed double phenylethynylation of 2,2′-dibromo-5,5′-dinitrobiphenyl (28) and 2,2′-diiodobiphenyl (34) have the fluorenyl structures 30b and 35b, respectively, rather than the phenanthrene structures 30a and 35a. Comparative spectra were also obtained for 9-(phenylethynyl)phenanthrene (38) (Reference 103) and 9-(3-phenyl-2-propynylidene)-fluorene (39a) (Reference 104). Other 9-alkylidenefluorenes have been reported (Reference 105).



(38)

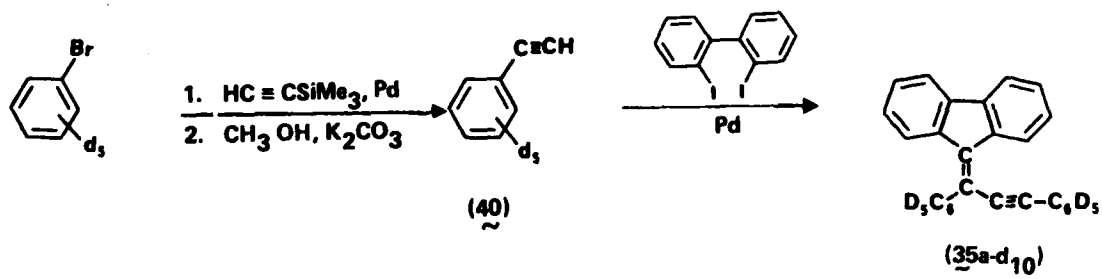


(39)

a: $R_1 = H, R_2 = C \equiv CPh$
b: $R_1 = R_2 = Ph$
c: $R_1 = R_2 = CH_3$
d: $R_1 = R_2 = CN$

Well-defined splitting patterns for the fluorenyl ring protons were observed for compounds 30b, 35b and 39a in their 60-MHz proton NMR spectra. Proton NMR spectra at 250-MHz were obtained for compounds 30b and 35b for detailed NMR analysis (Tables 1 and 2). Unambiguous assignment of chemical shifts to the respective fluorenyl protons was only possible, however, with the d_{10} analog of 35b. In the synthesis of the d_{10} analog, phenyl-d_5-acetylene (40) was first prepared from bromobenzene-d_5 (Reference 106). Reaction of

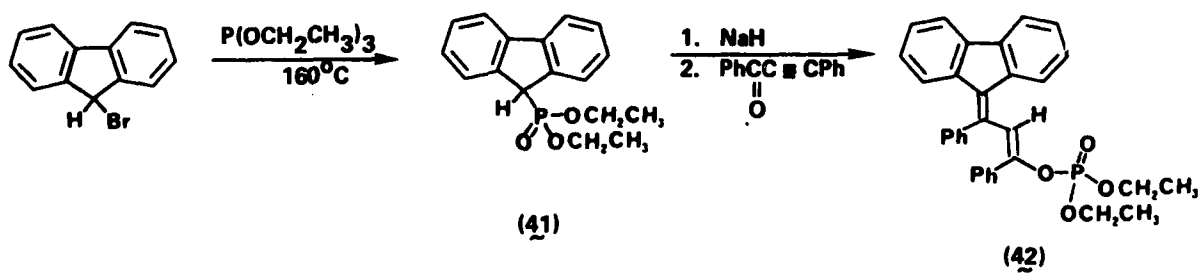
phenyl-d_5-acetylene with 2,2'-diiodobiphenyl (34) in the presence of palladium acetate and triphenylphosphine yielded the d_{10} derivative of 35b. The 250-MHz proton NMR spectrum of compound 35b-d_{10} showed only the splitting pattern of the fluorenyl protons. The chemical shift assignment was made on the basis of double resonance experiments (Table 1).



(40)

(35a-d_{10})

The fluorenylidene structure of 9-(3-phenyl-2-propynylidene)fluorene (35b) was further substantiated by an independent synthetic route starting with diethyl (fluoren-9-yl)phosphonate (41) which was prepared by the Michaelis-Arbusov reaction.



(41)

(42)

Under the Emmons-Wadsworth conditions, the phosphonate anion of 41 underwent conjugated addition with 1,3-diphenylpropynone to yield the yellow crystalline phosphate ester 42 which was characterized by 250-MHz proton magnetic resonance spectrometry (Table 2) and elemental analysis. On heating, 42 lost diethylphosphoric acid to give bright yellow crystals, which were identified as 35b by NMR, IR, MS and melting point (115°-116°C).

TABLE 1. 250-MHz PMR CHEMICAL SHIFT ASSIGNMENT OF FLUORENYL PROTONS IN COMPOUND 35b-d_{10}

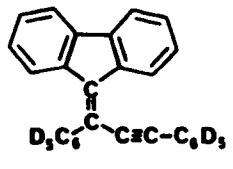
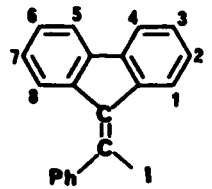
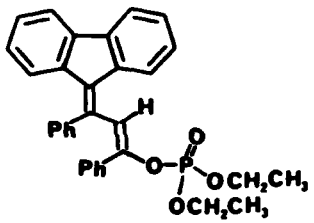
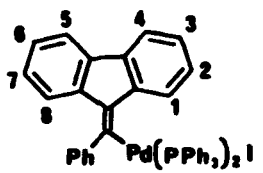
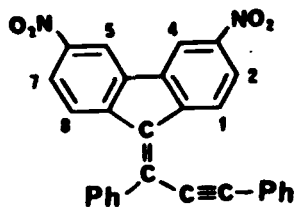
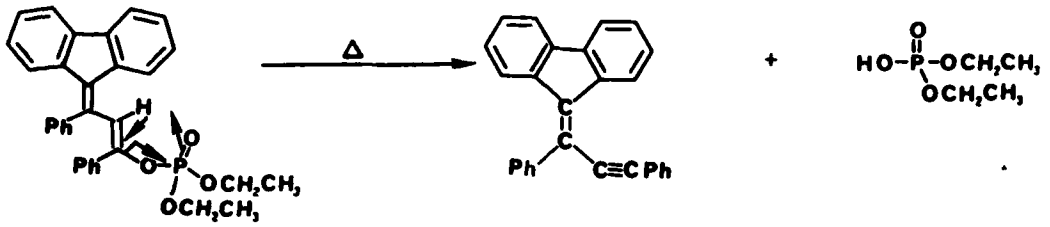
	H_1	$H_{2,3}$	H_4	H_5	H_6	H_7	H_8
δ	8.90–8.60	7.40–7.32	7.70–7.68	7.62	7.18	6.85	6.47
Multiplicity	m	overlapping multiplets	m	doublet $J_{5,6}$ = 7.5 Hz	dxdxd $J_{6,5}$ = 7.5 Hz $J_{6,7}$ = 8.0 Hz $J_{6,8}$ = 0.8 Hz	dxdxd $J_{7,5}$ = 1.1 Hz $J_{7,6}$ = 8.0 Hz $J_{7,8}$ = 8.0 Hz	dxd $J_{8,7}$ = 8.0 Hz $J_{8,6}$ = 0.8 Hz

TABLE 2. 250-MHz PMR CHEMICAL SHIFT ASSIGNMENT OF FLUORENYL DERIVATIVES STRUCTURALLY RELATED TO COMPOUND 35b

Compounds	δ Values (Multiplicity)							
	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8
	9.08-9.04 (m)	7.73-7.33 (overlapped with phenyl multiplet)		7.71	7.63 (dxd) J = 7.5 0.8	7.21 (dxdxd) J = 7.5 0.8 8.2	6.81 (dxdxd) J = 8.2 0.8 8.2	6.09 (dxd) J = 8.0 0.8
	8.27-8.17 (m)	7.65-7.44, 7.40-7.25, 7.20-7.06 (as 3 indistinguishable sets of multiplets overlapped with phenyl multiplet)				7.00 (dxdxd) J = 7.5 0.8 8.2	6.90 (dxdxd) J = 8.2 0.8 8.2	6.40 (dxd) J = 8.0 0.8
	9.87-9.83 (m)	6.48 (broad d) J = 7.5	6.84-7.67 (multiplets overlapped with phenyl multiplets)			6.65 (dxdxd) J = 7.5 7.5 8.0	6.48 (broad d) J = 7.5	6.36 (d) J = 7.5
	9.14 (d) J = 8.6	8.48 (dxd) J = 8.6 2.1	Not present	8.97 (d) J = 2.1	8.89 (d) J = 2.1	Not present	7.90 (dxd) J = 8.7 2.1	6.79 (d) J = 8.7



(42) (35b)

Mechanism of Formation of 9-(3-Phenyl-2-propynylidene)fluorene. The palladium-catalyzed coupling reaction (Heck reaction) of aryl halides with phenylacetylene is well known (References 25, 26, 94, 95, 101). Similarly, in the phenylethynylation reaction of 2,2'-diiodobiphenyl, the palladium[0] species generated in situ undergoes facile oxidative addition with one of the two carbon-iodine bonds in 2,2'-diiodobiphenyl. The resulting arylpalladium[II] complex then undergoes nucleophilic attack by a phenylacetylide anion, which is formed from phenylacetylene in the triethylamine solvent, giving complex 43.

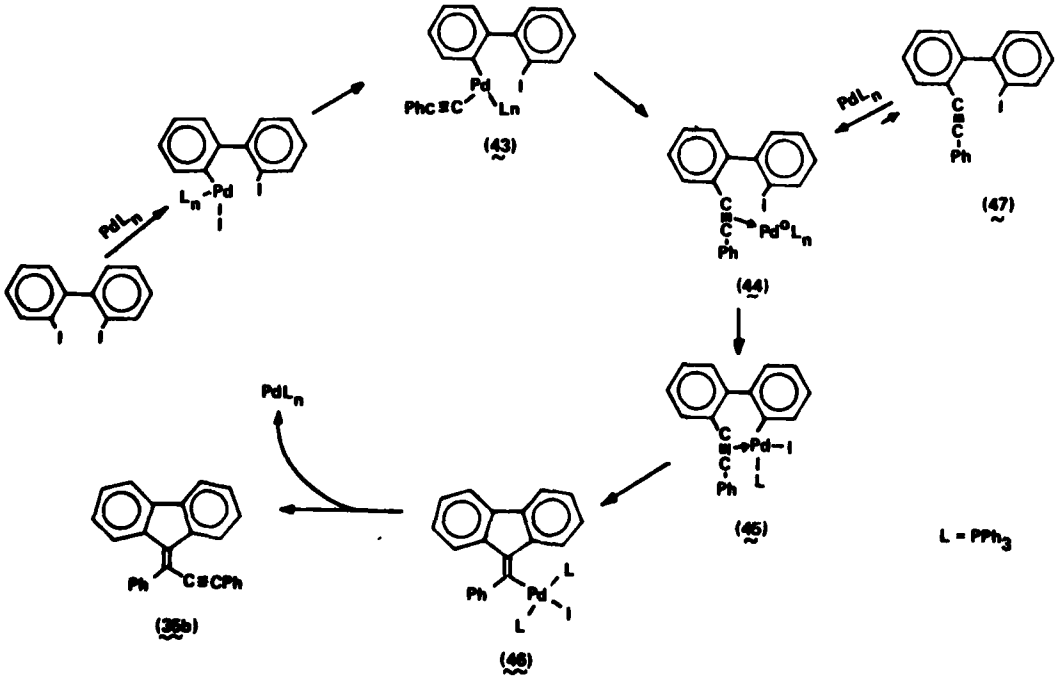


Figure 1. Mechanism of Formation of 9-(3-Phenyl-2-propynylidene)fluorene.

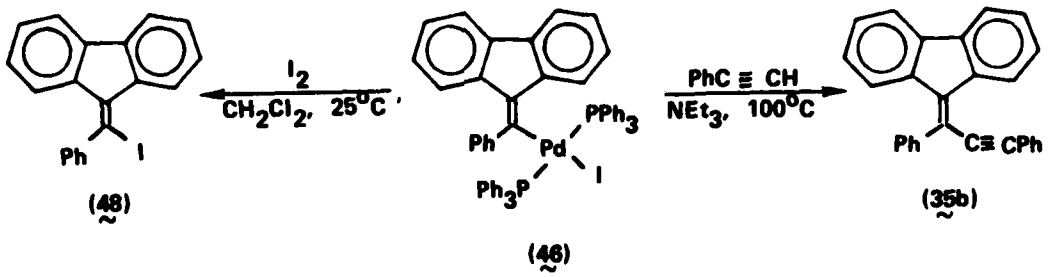
Through reductive elimination from complex 43, carbon-carbon bond formation takes place with concomitant regeneration of palladium[0], i.e., complex 44, which undergoes a second facile oxidative addition with the nearby carbon-iodine bond to give complex 45. Addition of the aryl palladium bond in complex 45 across the carbon-carbon triple bond (Reference 107) is facilitated by the proximity of the reacting functions and also by the formation of a thermodynamically favorable five-membered ring. The resulting (fluorenylidenebenzyl)palladium[II] complex 46 undergoes a straightforward sequence of nucleophilic attack by a phenylacetylide anion and then reductive elimination to yield the final product, i.e., compound 35b.

When 2,2'-diiodobiphenyl was treated with one equivalent of phenylacetylene in the presence of palladium acetate, the isolated product mixture comprised only 40% 35b and 44% unreacted starting material. The fact that no 2-iodo-2'-(phenylethynyl)biphenyl (47) (Reference 11) was detected indicated that the palladium[0] complex 44, generated from reductive elimination of complex 43, underwent oxidative addition with the proximal carbon-iodine bond faster than dissociation to yield 47.

The participation of complex 44 in the catalytic cycle was implicated by a separate experiment in which 47 was allowed to react with one equivalent of phenylacetylene in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium[0] (Reference 108) in triethylamine. A virtually quantitative yield of the fluorenyl compound 35b was obtained.

The (fluorenylidenebenzyl)palladium[II] complex 46 was synthesized by heating 47 and tetrakis(triphenylphosphine)palladium[0] in triethylamine. Characterization of the air-stable complex 46 was accomplished by 250-MHz proton magnetic resonance spectrometry (Table 2) and elemental analysis. That complex 46 undergoes a reaction with phenylacetylene to yield the fluorenylidene compound 35b clearly establishes the importance of complex 46 in the palladium-catalyzed phenylethynylation reaction of 2,2'-diiodibiphenyl (34).

As expected, complex 46 also undergoes electrophilic cleavage with iodine, yielding the iodo compound 48 (Table 2).



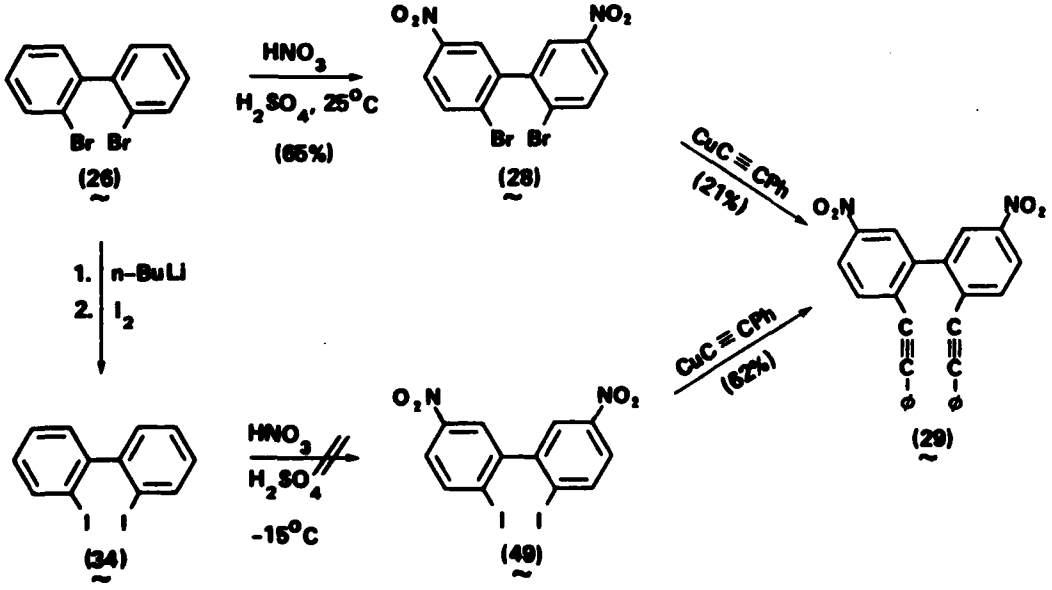
(48) (46) (35b)

It is interesting to note that formation of the alkylidenefluorene skeleton, i.e., compounds 30b and 35b, via palladium-catalyzed double phenylethynylation of 2,2′-dihalobiphenyl suggests a facile method for attaining fluorenones and fluorenes with unusual substitution patterns. For example, 3,6-dinitrofluorenone, which cannot be synthesized by conventional nitration, can be obtained via an alkene oxidation reaction of the alkylidenefluorene, 30b.

Nitration of 2,2′-Diiodobiphenyl

2,2′-Diiodo-5,5′-dinitrobiphenyl (49) underwent double phenylethynylation with a stoichiometric amount of cuprous phenylacetylide to give a 52% yield of 29 (Reference 15). In our hands, the yield was about 62%. A comparative experiment using 2,2′-dibromo-5,5′-dinitrobiphenyl (28) yielded only 20.6% of 29 among tarry intractable materials. This striking disparity in reactivity between the dibromo and the diiodo compounds necessitated the transformation of 2,2′-dibromobiphenyl to 2,2′-diiodobiphenyl (34) (Reference 11) prior to nitration en route to (49).

Although in the dinitration of 2,2′-dibromophenyl (26) in sulfuric acid at 0°C, the dibromo compound 28 was obtained in 65% yield, the dinitration of 34 under the same conditions (even at −15°C) gave a solid which was amorphous and insoluble in all common solvents. The mp observed was >280°C and the infrared spectrum showed strong hydroxy absorptions. We speculate that oxidation at the carbon-iodine bonds probably has taken place.



To circumvent the apparent problem of oxidation-hydrolysis of the carbon-iodine bonds of 34 during nitration in concentrated sulfuric acid, we examined the feasibility of nitration in a mildly acidic-to-neutral medium. The nitronium salt approach offers an attractive solution to the problem. Besides avoiding the use of a strong acid as reaction medium, this method also allows precise determination of the stoichiometry of the nitrating agent. Thus, nitronium tetrafluoroborate effectively nitrates 2-tolunitrile to yield 3,5-dinitrotolunitrile without causing hydrolysis of the nitrile function (Reference 109). The commercial availability of nitronium tetrafluoroborate (Aldrich) in sulfolane solution allowed us to examine this possibility. 2,2'-Diiodobiphenyl (34) was allowed to react with nitronium tetrafluoroborate, which was in 5% excess. Thin layer chromatography on silica gel showed that nitration indeed took place, although not cleanly. Hydrolytic work-up turned out to be extremely tedious and this method was abandoned.

Various other nitronium salts are known, for example, nitronium hexafluorosilicate (Reference 110), nitronium hexafluorophosphate (Reference 111) and nitronium trifluoromethanesulfonate(triflate) (References 112–117). It was shown that nitronium triflate (50) is the most reactive reagent. Several preparative procedures have been reported.

1. $N_2O_5 + (CF_3SO_2)_2O \xrightarrow[-20°C]{\text{neat}} \xrightarrow[2\text{ hr.}]{60°C} \underset{50}{NO_2^{\oplus}CF_3SO_3^{\ominus}}$ (100%) (Reference 112)

2. $N_2O_5 + (CF_3SO_2)_2O \xrightarrow[-20°C]{\text{neat}} \xrightarrow[20\text{ hr.}]{0°C}$ 50 (68%) (Reference 113)

3. $NO_2Cl + CF_3SO_3H \xrightarrow[-78°C]{\text{neat}} \xrightarrow[\text{overnight}]{25°C}$ 50 (100%) + HCl (Reference 114)

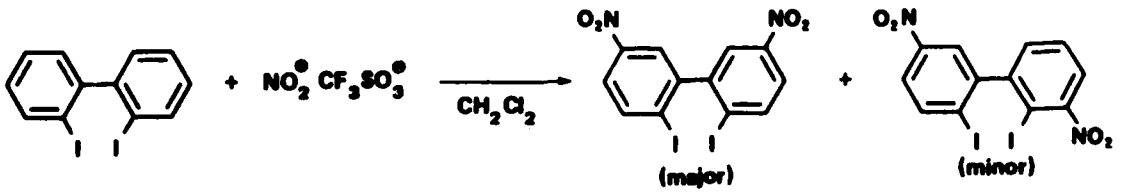
4. $N_2O_5 + CF_3SO_3H \xrightarrow[20\text{-}35°C]{ClCH_2CH_2Cl}$ 50 (97%) + HNO_3 (References 115, 116)

5. $HNO_3 + 2CF_3SO_3H \xrightarrow[25°C]{\text{neat or } CH_2Cl_2}$ 50 (100%) + $H_3O^{\oplus}CF_3SO_3^{\ominus}$ (Reference 117)

The procedures involving the preparation of dinitrogen pentoxide require the use of ozone to prevent detonation hazards. In the synthesis using nitryl chloride, gaseous hydrogen chloride must be vented frequently from the reaction mixture to ensure completion of the reaction. Procedure 5 thus appears to be the most convenient and suggests minimal difficulty in scale-up. Two equivalents of triflic acid and one of anhydrous nitric acid react to form a white, crystalline solid mixture of nitronium triflate (50) and hydronium triflate. 2,2'-Diiodobiphenyl (34) was added to a dichloromethane suspension of the triflate mixture at 0°C. The mixture was stirred at 25°C for 2–4 hours before hydrolytic work-up. An 89% crude yield of the nitration product was realized. The desired pure 2,2'-diiodo-5,5'-dinitrobiphenyl (49) was obtained by recrystallization.

We favored an alternative procedure for the in situ generation of nitronium triflate. Anhydrous nitric acid (obtained from distillation of fuming nitric acid from concentrated sulfuric acid) was added to triflic anhydride in dichloromethane. No precipitate was formed. The homogeneous yellow solution contained soluble nitronium triflate. The addition of 2,2′-diiodobiphenyl as a dichloromethane solution at 25°C and subsequent work-up afforded a 64% yield of 49 after recrystallization. The mother liquor from the recrystallization contained a mixture of 49 and its corresponding 3,5′-dinitro isomer. High performance liquid chromatography and proton NMR spectrometry indicated that only these two isomers were formed.

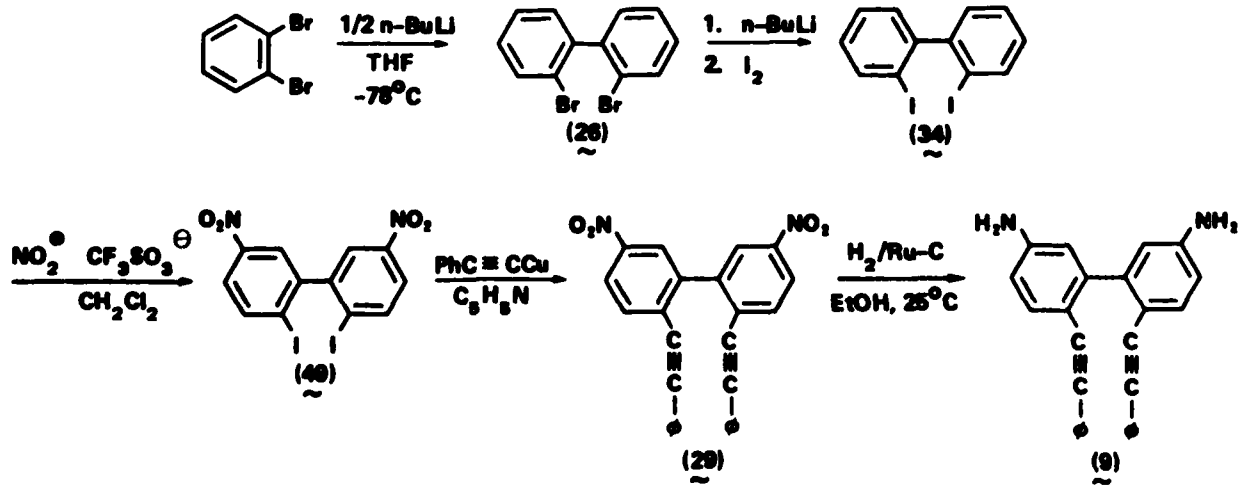
$$HNO_3 + (CF_3SO_2)_2O \longrightarrow NO_2^{\oplus}\ CF_3SO_3^{\ominus} + HOSO_2CF_3$$



Apparently, the isomer ratio was not affected by temperature variation. The experiments performed at 25°C, 0°C and −20°C afforded essentially the same yield for the desired isomer 49. Carrying out the experiment at −78°C resulted in no appreciable reaction after 2 days.

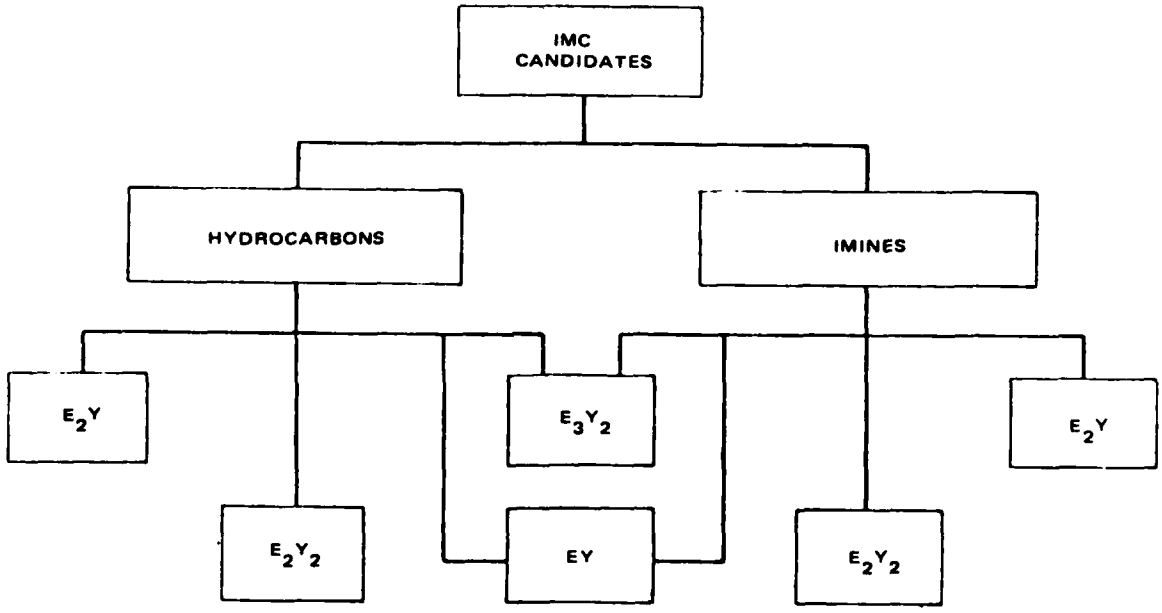
The nitro compound 49 was converted to 2,2′-bis(phenylethynyl)-5,5′-dinitrobiphenyl (29) by the copper[I] phenylacetylide method, giving a 62% yield. Hydrogenation of 29 (Reference 118) resulted in selective reduction of the nitro groups, thus completing the synthesis of 2,2′-bis(phenylethynyl)-5,5′-diaminobiphenyl (9). The sequence is summarized in Scheme 5.

Scheme 5



2. TASK II: SYNTHESIS AND THERMAL REACTION OF NOVEL IMC SYSTEMS

Consideration of pertinent literature permits certain generalizations regarding linear organic systems which would likely undergo thermal intramolecular cyclization (IMC) to give highly fused aromatic and/or heteroaromatic structures. Polyenes and -ynes are promising candidates. Of paramount significance are the geometric dispositions of such unsaturated systems, i.e., cis-trans isomerism and proximity of interacting unsaturation sites. More importantly, cyclization must not generate volatile by-products. The chemical systems surveyed can be categorized according to the flow chart below. Systems in each category were evaluated for their potential as IMC candidates.

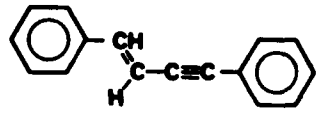


EY = enynes; E_2Y = dienynes; E_2Y_2 = diendiynes; E_3Y_2 = triendiynes

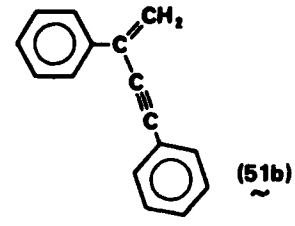
The EY Systems

The Straus and inverse-Straus coupling products have been postulated as intermediary compounds in the thermal curing of acetylene-terminating quinoxalines (Reference 6). Some

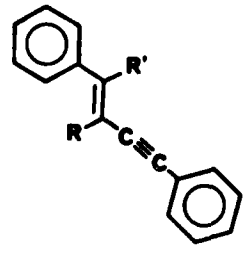
systems containing the Straus and inverse-Straus skeletons (51) have been investigated. As described above (see page 5), the incorporation of enyne units (51a) in polymer systems did not bring about intramolecular cyclization during thermal cure. The investigation of 51b has thus far been discouraged by the difficulty of its isolation. The fact that a large proportion of polymeric material was always obtained from reaction mixtures of 51b probably is indicative of a low-energy polymerization pathway for 51b.



(51a)

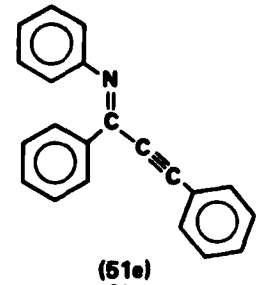


(51b)



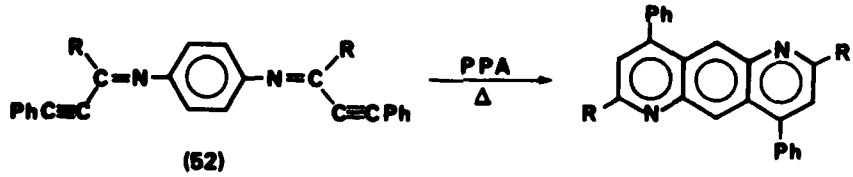
(51c) R = Ph, R' = H

(51d) R = H, R' = Ph

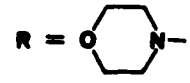


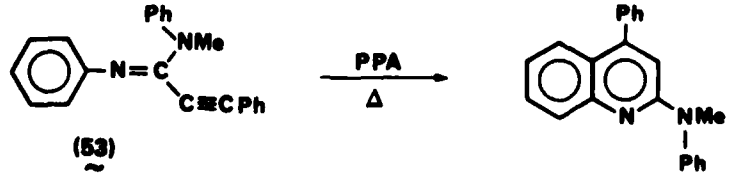
(51e)

It is interesting to note that the EY-imine systems 52 and 53 undergo intramolecular cyclization reactions in polyphosphoric acid (References 119, 120).



(52)

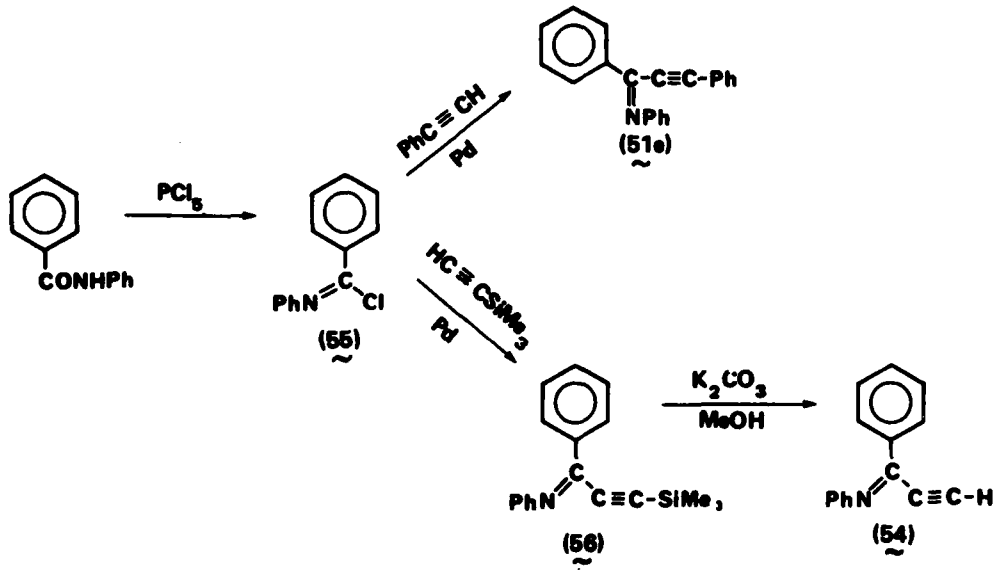




(53)

Both 52 and 53 are very similar to 1,3-diphenylpropynone anil (51e) in structure. With the expectation that 51e would undergo an analogous IMC reaction, we carried out the synthesis of (51e) and propiolophenone anil (54) (Scheme 6).

Scheme 6



Our methods of synthesis for 51e and 54 have a common imidoyl chloride (55), which was synthesized by treatment of benzanilide with phosphorus pentachloride (References 121, 122), and isolated by distillation in 90.1% yield (bp 120–125°C/0.1 torr; mp 40–40.5°C). Conversion of 55 to 51e (mp 60.5–61°C) was uneventful via the Heck phenylethynylation procedure (Reference 25).

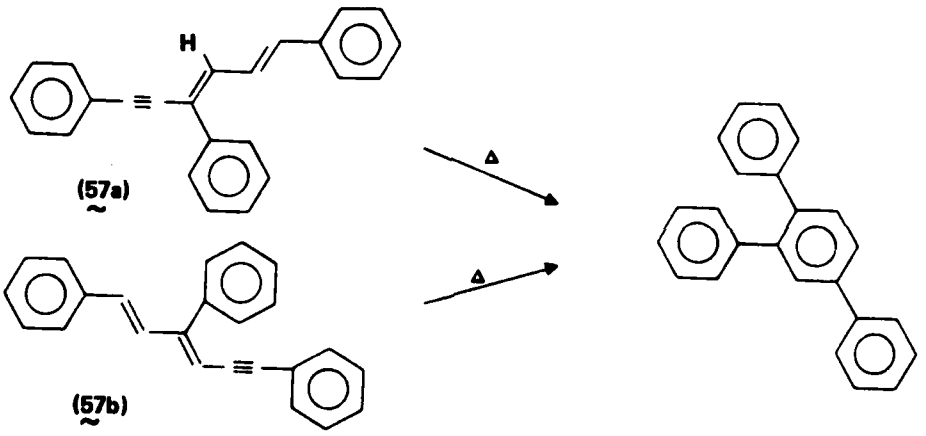
Compound 54 was synthesized via palladium-catalyzed ethynylation using ethynyltrimethylsilane (Reference 106). Characterization of the new compounds 54 and 56 by IR, NMR, MS and combustion analysis was complete (compound 54: mp 117–118°C; compound 56: bp 130–135°C/0.1 torr).

Differential scanning calorimetric (DSC) analysis of 51e indicated an intense melting endotherm at 61°C and another broad but shallow endotherm at 265°C. There was no reaction exotherm detectable. This observation was in agreement with the fact that heating a sample of 51e at 210°C in diphenyl ether for 30 hours promoted no reaction. On the other hand, the DSC curve of 54 showed a moderate exotherm at 197°C. But unfortunately, only polymeric/oligomeric material was isolated from the thermal reaction of 54. Intramolecular cyclization did not occur.

The E_2Y-Hydrocarbon Systems

The dienyne systems such as 57a and 57b can conceivably be incorporated in polymer chains to contribute to their flexibility and thus better processibility (e.g., lowering of Tg). The dangling effect of the branching group also results in added flexibility. Thermal treatment of these dienyne units was expected to give terphenyl structures. Interestingly, both monomeric dienynes 57a and 57b could cyclize to the same quaterphenyl. Different modes of difunctionalization on the terminal rings of the dienynes may lead to straight-chain or angular type catenations during polymerization.

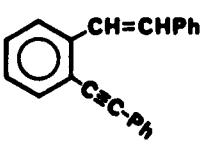
Both monomeric 57a and 57b have been synthesized. They underwent extensive polymerization upon heating either in hot tetralin or without solvent. No cyclization product was detected (Reference 123). Thus intramolecular cyclization schemes involving hydrocarbon dienyne type structures 57a and 57b are considered unlikely to succeed.



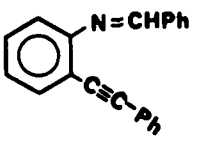
(57a) (57b)

The Hetero-E_2Y Systems

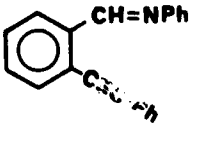
E_2Y systems having one of the double bonds as part of an aromatic ring (58) are expected to cyclize thermally into naphthalene-like structures. The ortho relationship of the two ends of the E_2Y system is tantamount to the cis configuration about a double bond.



(58a)

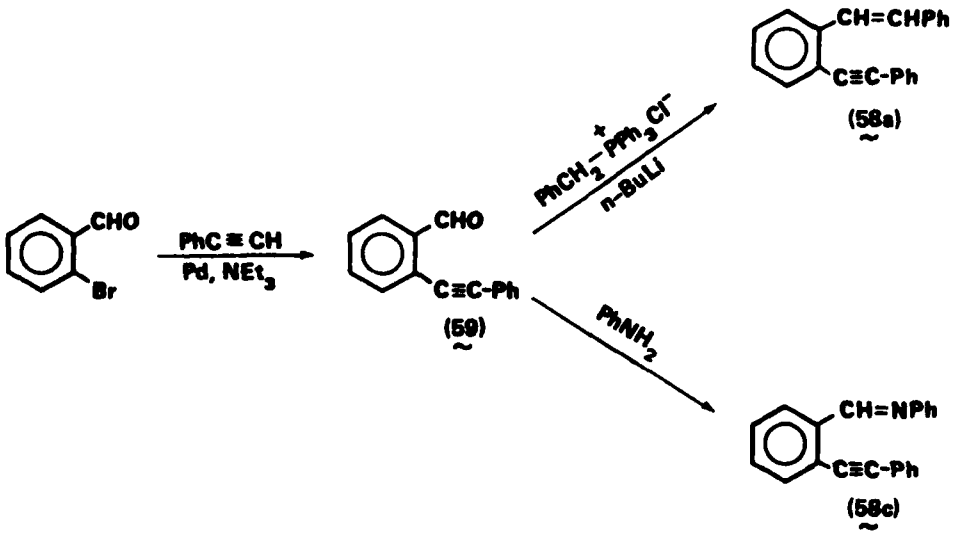


(58b)

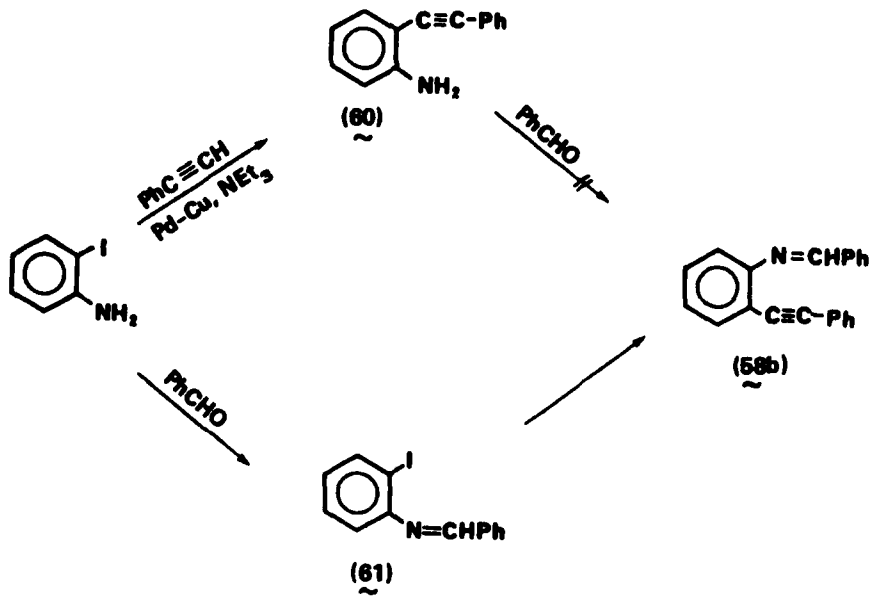


(58c)

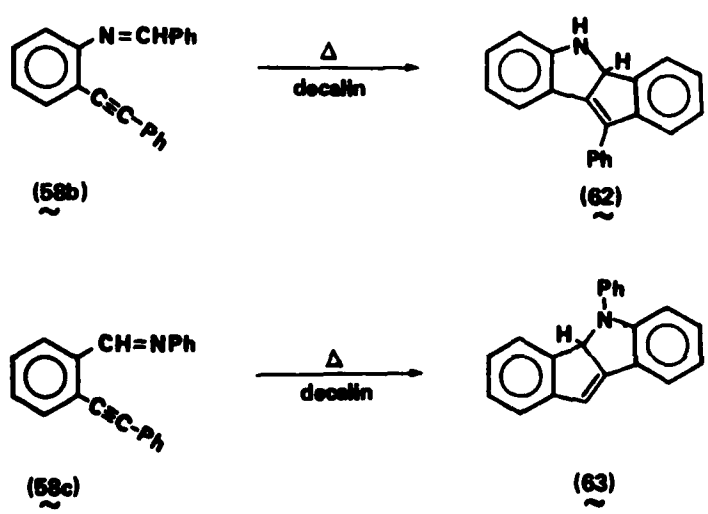
We have established that both 58a (Reference 124) and 58c can be obtained from the same aldehyde intermediate 59 (Reference 124), which follows from commercially available 2-bromobenzaldehyde via the Heck phenylethynylation reaction. The alternative method using the $(Ph_3P)_2PdCl_2/Cu_2I_2$ catalytic system (Reference 26) was found to be inefficient. The stilbene compound 58a was conveniently prepared by the Wittig olefination reaction. An alternative route involving the palladium-catalyzed coupling of 2-iodotolane and styrene is conceivable (Reference 101) but was not attempted in this work.



2-Aminotolane (60) (Reference 28) is a logical precursor to the imine 58b. Unfortunately, it fails to react with benzaldehyde for reasons probably more electronic than steric, since 59 undergoes facile imine formation with aniline. The iodoimine 61 (Reference 125) was successfully prepared from commercially available 2-iodoaniline and converted to the desired E_2Y-imine 58b by the copper-promoted palladium-catalyzed phenylethynylation reaction (Reference 26). The purification of 58b was problematic owing to its instability toward silica gel, alumina and Florisil column chromatography, benzaldehyde and 2-aminotolane (60) being recovered as the products of hydrolysis of 58b. Cellulose must be used as the chromatographic material.

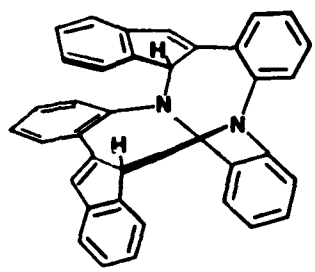


Although the hydrocarbon E_2Y system 58a failed to undergo cyclization reaction, each of the E_2Y-imines 58b and 58c yielded its corresponding isomer upon heating in hot tetralin. The reaction products 62 and 63 were assigned the indeno[1,2-b]indole structures based on their high melting points, elemental analysis, IR, NMR and MS characteristics.



Both 62 and 63 are higher melting than their respective starting materials 58b and 58c by nearly 200°C. It is conceivable that the incorporation of units such as 58b and 58c in a resin system can lead to significant lowering of the melting temperature by virtue of the flexible skeleton imparted by these substituent groups. Thermal curing of the resin would be expected to bring about a substantial enhancement in Tg due to the formation of rigid heterocyclic ring structures 62 and 63. However, the reaction yields were low.

The thermal reaction of 58c appears to be complex. While isomerization to 63 occurred in decalin solvent, transformation to a dimeric structure took place when 58c was heated at 210°C in diphenyl ether. Mass spectrometric analysis established that the product was not isomeric to 58c. The NMR spectrum showed only aromatic protons. The infrared spectrum, the mass spectrometric fragmentation pattern and the high mp were supportive of a condensed ring system. The observed molecular ion at m/e 487 suggested a mass loss of 75 from a dimeric product (expected MW 562) of 58c. We propose a tentative structure for the dimeric product as follows:

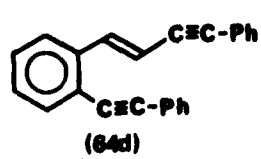


The low-yield thermal reactions that 58b and 58c undergo render these compounds unattractive for potential application to IMC reactive polymers.

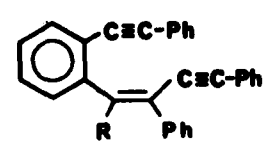
The E_2Y_2-Hydrocarbon Systems

Structurally, the state-of-the-art bis(phenylethynyl)biphenyl system (64a) is a member of the E_2Y_2 group which comprises compound 64 having the basic skeleton of cis, cis-octa-3,5-dien-1,7-diyne.

(64) a. $R_1 + R_2 = C_4H_4$
b. R_1 = Ph, R_2 = H
c. $R_1 = R_2$ = Ph



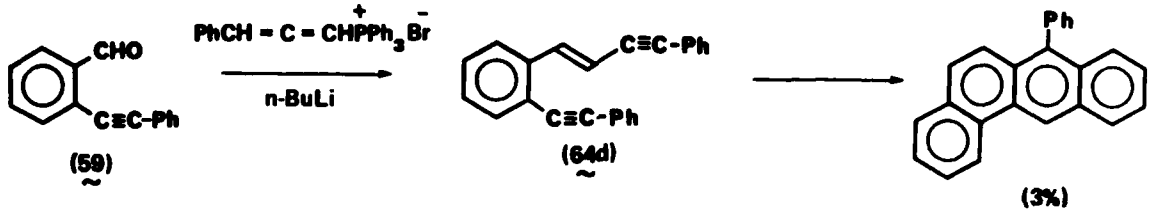
(64d)



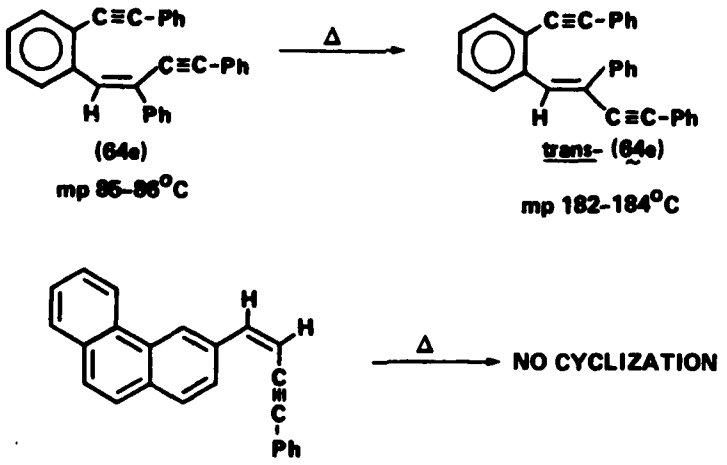
(64e) R = H

(64f) R = Ph

Compound 64d was synthesized by a Wittig reaction of 2-(phenylethynyl)benzaldehyde (59) with the ylide from (3-phenyl-1,2-propadienyl)triphenylphosphonium bromide. Preliminary studies on compound trans-64d revealed that heating in hot tetralin (150–200°C) under nitrogen was not sufficient to promote trans to cis isomerization about the double bond so that the phenylethynyl pendants could be brought into close proximity to each other. A 3% yield of a highly crystalline material was obtained together with recovered starting material. Infrared and mass spectra and the high mp of 192–193°C (compound 64d is an oil at room temperature) of the product were consistent with a condensed aromatic structure, probably the result of an inefficient IMC reaction.

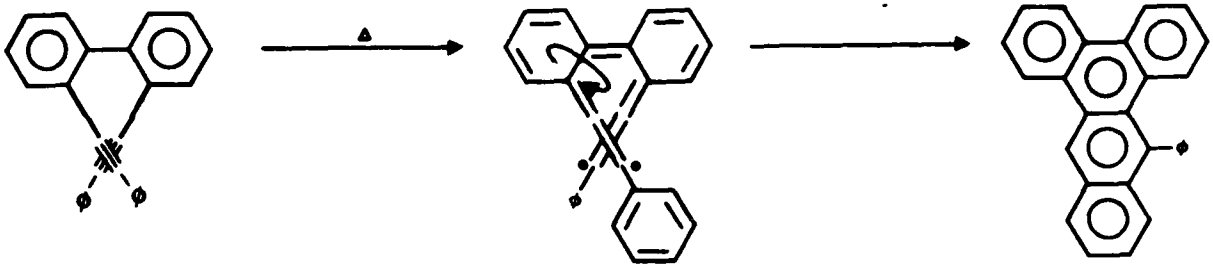


We have also observed that compound 64e undergoes only cis-trans isomerization in tetralin at reflux. The facile isomerization can be explained by a mechanism involving thermally generated bisallenic diradicals (Reference 123). The failure of a structurally similar system (Reference 126) to undergo thermal cyclization is probably also the result of a similar energy wasting pathway via a diradical mechanism.

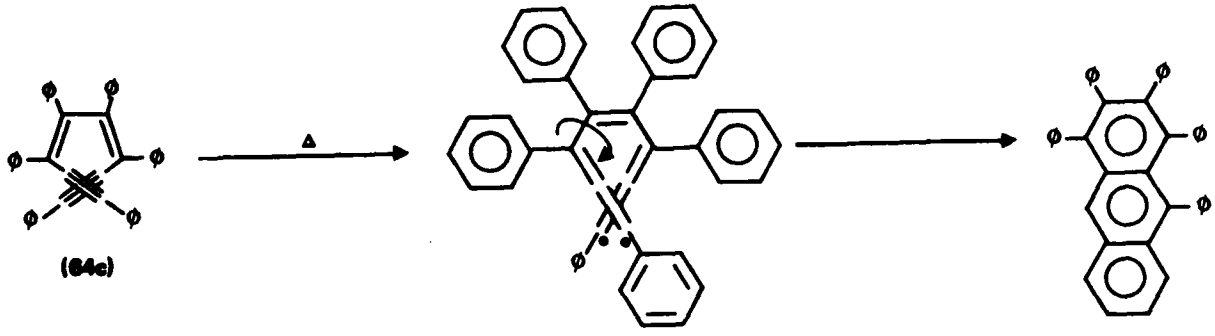


(Reference 126)

On the basis of the bisallenic diradical hypothesis, it is possible to interpret that the successful thermal IMC reaction of 64a rests in the formation of a similar bisallenic diradical being deprived of the possibility of a cis-trans isomerization process. It follows that the

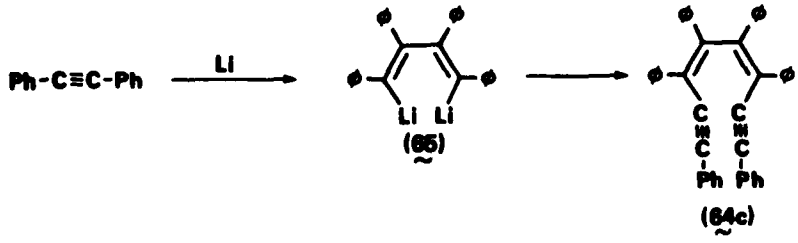


hexaphenylated cis, cis-octa-3,5-dien-1,7-diyne system 64c would be expected to give a bisallenic diradical intermediate which must overcome a high energy barrier for cis-trans isomerization due to steric reasons. Closure of the diradical in the cisoid conformation to the fused ring skeleton thus becomes kinetically competitive.



(64c)

Compound 64c bears remarkable structural similarity to the state-of-the-art biphenyl system (64a) but lacks the rigidity of the latter. Its incorporation into a polymer chain could be expected to add considerable flexibility in relation to biphenylic 64a. A two-step one-pot synthesis from diphenylacetylene starting material seems to be an obvious procedure leading to 64c. The merit of this approach lies in the convenient preparation of the dilithio tetraphenylbutadiene compound (References 127, 128). We have examined several approaches in the conversion of the dilithio tetraphenylbutadiene compound (65) into 64c.

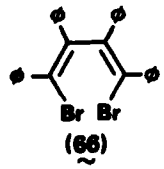


(65)

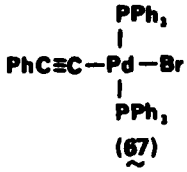
(64c)

The dilithio compound underwent lithium-halogen exchange instead of displacement with bromophenylacetylene (Reference 129) due to the positive character of the bromine on 1-bromo-2-phenylacetylene. The reaction product of the lithium-bromine exchange reaction

was identified as 1,4-dibromo-1,2,3,4-tetraphenylbutadiene (66) by comparison of its IR spectrum and melting point (146–148°C) with those of an authentic sample synthesized by treatment of the dilithio compound (65) with carbon tetrabromide (Reference 123).



(66)

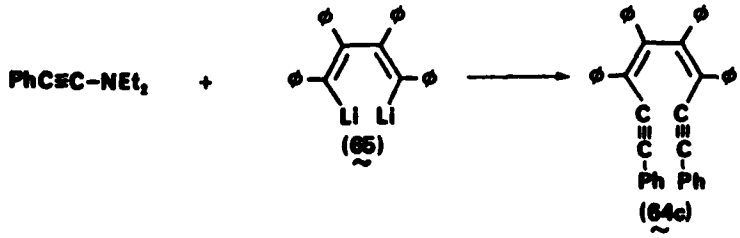


(67)

Neither the displacement of bromine atoms in 66 with lithium acetylide nor the palladium-catalyzed coupling of 66 (or its iodo analog) with phenylacetylene took place. We examined the possibility of the reaction between 65 and bromo(phenylethynyl)bis(triphenylphosphine)palladium[II] (67) as an entry to 64c. The palladium complex 67 was easily synthesized via the oxidative addition (Reference 130) of bromophenylacetylene to tetrakis-(triphenylphosphine)palladium[0] (Reference 108). Treatment of the palladium complex 67 with the dilithio compound 65 in tetrahydrofuran caused an immediate darkening of the solution mixture. Thin layer chromatography showed that the reaction was more complex than expected and further investigation was abandoned.

An alternative approach to the synthesis of 64c was by treatment of 65 with phenylacetyl chloride. This method also proved to be unsuccessful, however. Work-up of the mixture yielded 1,2,3,4-tetraphenylbutadiene and phenylacetic acid.

An ynamine intermediate (Reference 131) may be feasible for the synthesis of 64c, although we have not completed this study. The experimental results obtained suggest that

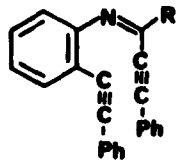


(65) (64c)

there is a more severe steric crowding for the terminal substituents on the tetraphenylbutadiene unit than the 2,2′-positions of biphenyl. Space-filling models seem to support this interpretation.

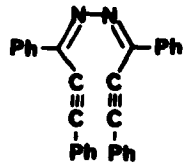
The Hetero-E_2Y_2 Systems

Our effort was then directed to examine a few selected hetero-E_2Y_2 systems (64g, 64h, 64i, 64j, 64k, 64m).

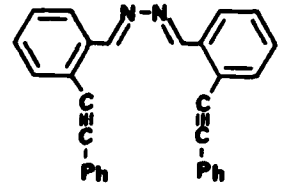


(64g) R = H

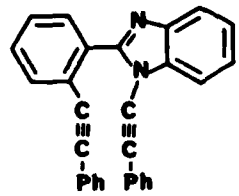
(64h) R = Ph



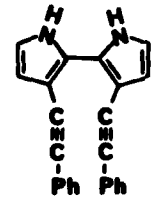
(64i)



(64j)



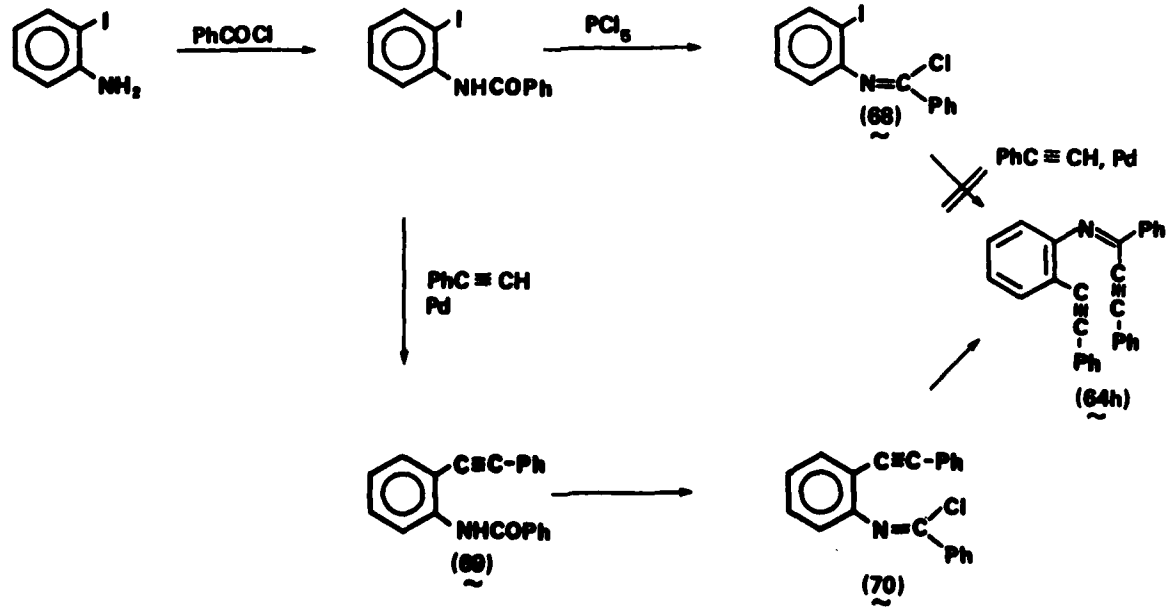
(64k)



(64m)

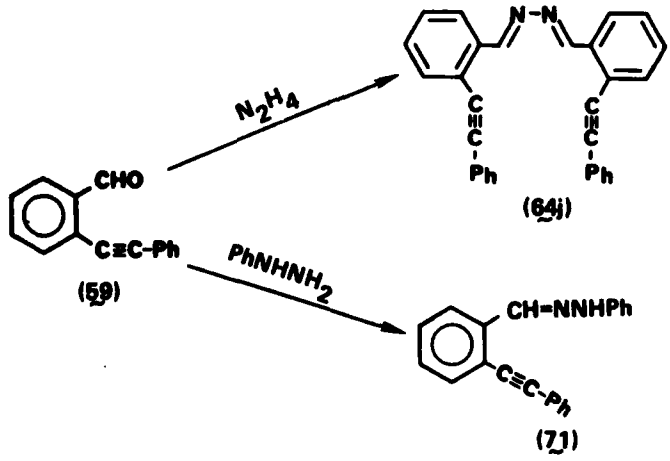
In the synthesis of the E_2Y_2-imine compound 64h, the most direct approach would be the imine formation between 2-aminotolane and 1,3-diphenyl-2-propynone. The method is however judged infeasible since the amino group on 2-aminotolane lacks the nucleophilicity of aniline and 1,3-diphenyl-2-propynone undergoes nucleophilic attack in the Michael 1,4-manner. Scheme 7 depicts a likely approach to the synthesis of 64h, the preparation of the imidoyl chloride compound 68 being the key step.

Scheme 7



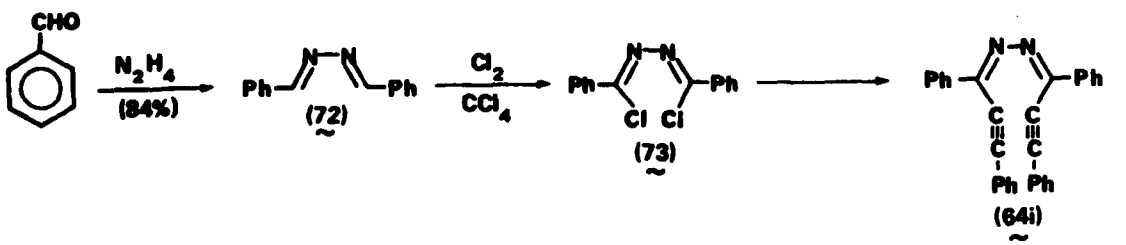
Compound 68 was synthesized in 56% overall yield in two steps from a commercially available starting material. Double phenylethynylation of 68 in the presence of the palladium acetate-triphenylphosphine catalyst did not take place due to an apparent decomposition of some palladium[0] intermediates formed in situ. It has been suggested that extra triphenylphosphine in the reaction mixture helps to stabilize the intermediate Pd[0] species, which can be generated alternatively by the reduction of dichlorobis(triphenylphosphine)palladium[II] with copper[I] iodide. Toward this end, we treated compound 68 with phenylacetylene in the presence of the new catalyst system. The reaction again was incomplete. We then examined the feasibility of the alternate path which involves going through phenylethynylation in two separate steps. Synthesis of the intermediate compound, N-(benzoyl)-2-aminotolane (69), was uneventful but the purification of the subsequent compound 70 was tedious. Further experimentation would be needed to improve on the process and prepare 64h.

Concurrently with the attempted synthesis of 64h, we also evaluated the procedure leading to compounds 64i and 64j. The synthesis of IMC-benzalazine 64j was accomplished in two steps and in high yields from commercially available 2-bromobenzaldehyde, which underwent a conventional phenylethynylation to yield 2-(phenylethynyl)benzaldehyde (59) (Reference 124). The subsequent reaction of 59 with hydrazine afforded IMC-benzalazine 64j. An equally facile reaction was the preparation of 2-(phenylethynyl)benzaldehyde phenylhydrazone (71). Differential calorimetric scanning (DSC) analyses indicated reaction exotherms for both 64j (Tmax = 190°C) and 71 (Tmax = 230°C). Upon heating these compounds at 200°C, the fast disappearance of the starting materials was striking. Unfortunately, no cyclization product was obtained in either case. Only extensive polymerization took place.

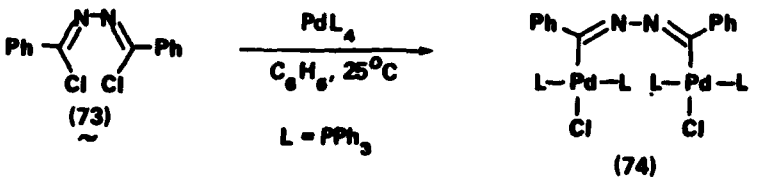


Synthesis of 1,4-bis(phenylethynyl)-1,4-diphenyl-2,3-diazabutadiene (64i) is outlined in Scheme 8. Condensation of two moles of benzaldehyde and one mole of hydrazine hydrate in absolute ethanol gave bright yellow crystals of benzalazine (72) in good yields (Reference 132). Chlorination of benzalazine was difficult to monitor (References 133, 134), but we were able to obtain pure samples of 1,4-dichloro-1,4-diphenyl-2,3-diazabutadiene (73). The alternative approach to 73, i.e., via chlorination of 1,2-dibenzoylhydrazine (References 135, 136) with thionyl chloride, led to 2,5-diphenyl-1,3,4-oxadiazole instead of 73. Phenylethynylation using the Heck catalyst (Reference 25) resulted in incomplete conversion and a large amount

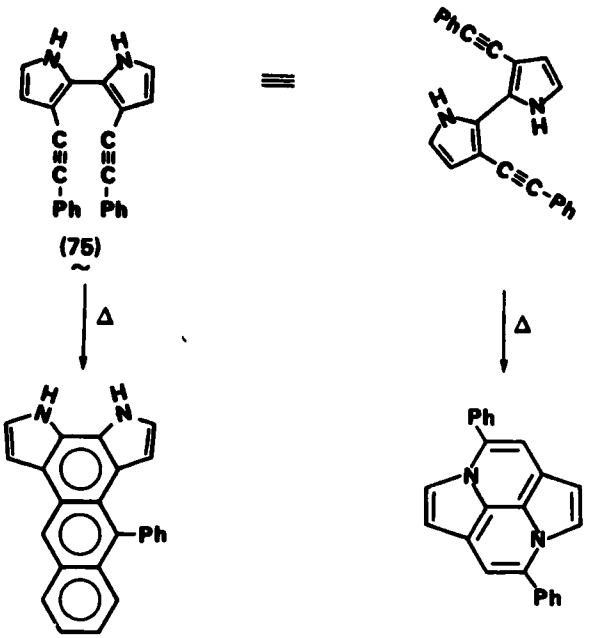
Scheme 8



of tarry residue appeared. Further experiments are needed to determine the cause for the observed deviation from normalcy. An apparent possibility in circumventing the technical problem would be to pre-synthesize the intermediate palladium[II] complex (74) by a conventional oxidative addition reaction (Reference 130), and then to treat complex 74 with phenylacetylene.

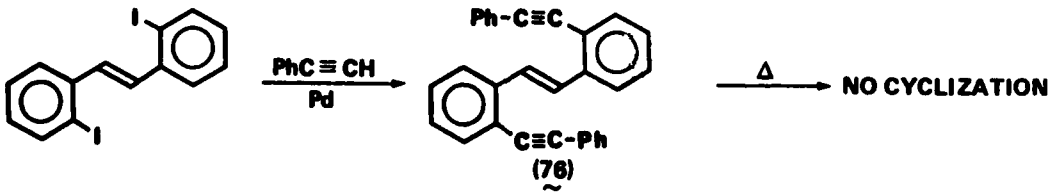


The availability of synthetic methods for the construction of 2,2'-bipyrroles (Reference 137) should make 75 an attractive candidate as an E_2Y_2–IMC system. The interesting possibility of a dual cyclization pathway for 75 is evident. This has not been investigated, however.

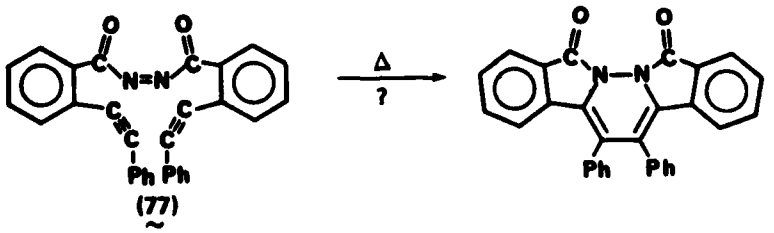


The E_3Y_2 Systems

Only one hydrocarbon compound (76) in this group has been prepared and studied. Treatment of 76 with heat did not effect intramolecular cyclization.

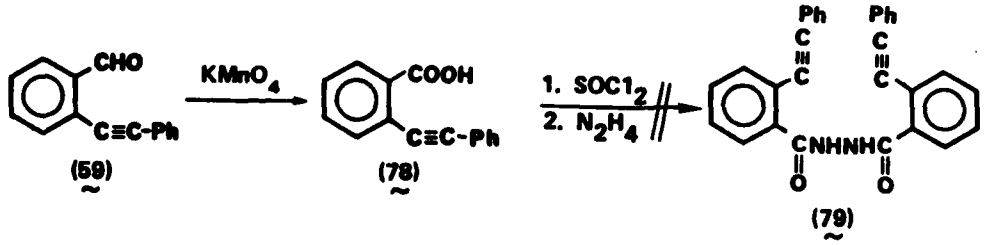


Diazine compounds are known to participate in Diels-Alder type cyclization reactions. The expectation that a plausible intramolecular [2+2+2] six-centered cyclization would take place between the nitrogen-nitrogen double bond in the diazine unit of compound 77 and the two proximal acetylene functions justified a synthetic attempt to obtain compound 77.



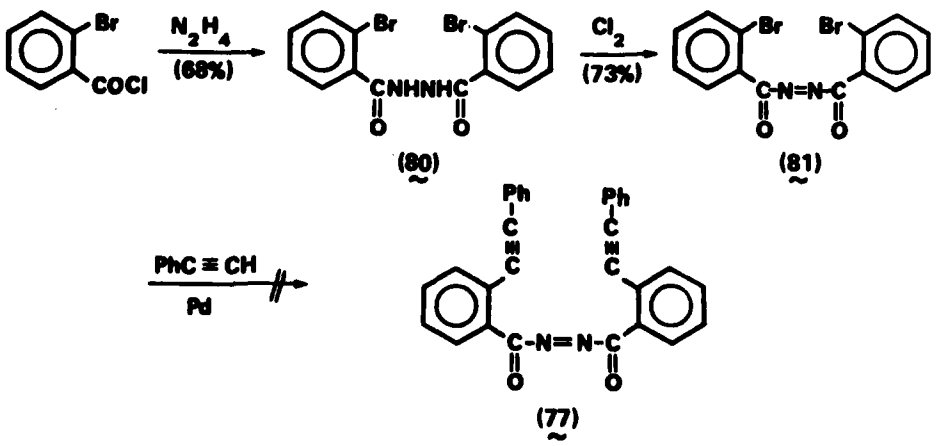
Our initial approach (Scheme 9) began with commercially available 2-bromobenzaldehyde from which 2-(phenylethynyl)benzaldehyde (59) was synthesized. Oxidation of 59 with aqueous potassium permanganate under neutral conditions yielded 2-(phenylethynyl)-benzoic acid 78 (Reference 138). Treatment of 78 with thionyl chloride afforded the corresponding acid chloride which readily underwent a reaction with hydrazine hydrate. The isolated major product, however, was not the expected 79. Further investigation was abandoned.

Scheme 9

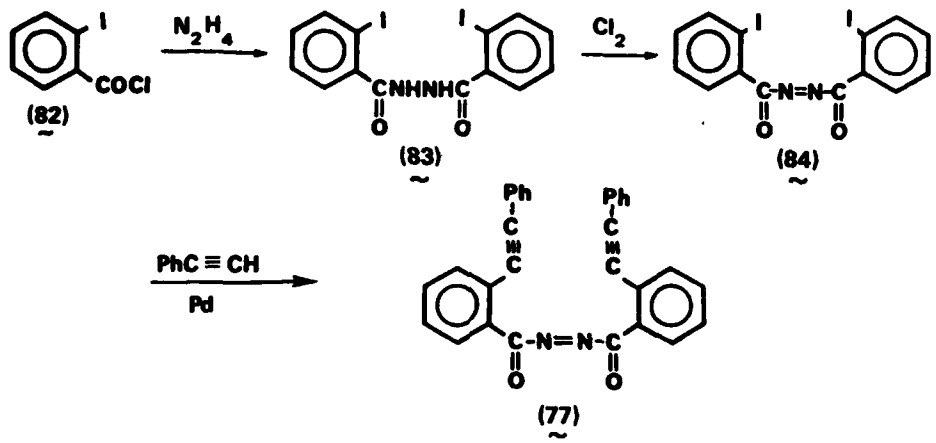


An alternative approach is depicted in Scheme 10. The required starting material 1,2-bis(2-bromobenzoyl)hydrazine (80) was synthesized from commercially available 2-bromobenzoyl chloride (Reference 134). Oxidation of the hydrazine unit to the diazine was accomplished by treatment with chlorine gas. A good yield of 1,2-bis(2-bromobenzoyl)diazine (81) was realized. Difficulties encountered during the double phenylethynylation step have prevented us from attaining the ultimate target compound (77).

Scheme 10

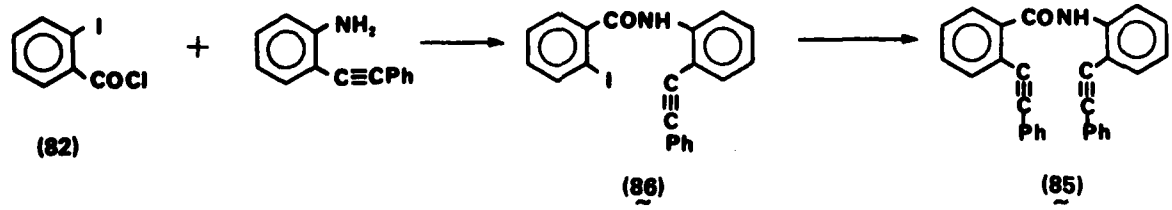


The synthetic approach outlined in Scheme 10 was examined using the iodo analogs. 2-Iodobenzoyl chloride (82) was synthesized from commercially available 2-iodobenzoic acid in 65% purified yield, and then allowed to react with hydrazine hydrate to give 1,2-bis(2-iodobenzoyl)hydrazine (83). Further steps leading to diazine 84 and finally 77 have not been undertaken.



Aromatic Amides with Phenylethynyl Pendants and Related Systems

Aromatic amides and hydrazides derived from 2-(phenylethynyl)benzoic acid (78) are structurally interesting due to the proximity of the acetylene bond and the nitrogen atom. Compound 85 was synthesized in two steps from 2-iodobenzoyl chloride (82). Compound 85 and its precursor 86 were characterized. The conversion of 86 to 85 was accomplished by a conventional palladium-catalyzed phenylethynylation.



Differential scanning calorimetric analysis (Figure 2) of compound 85 revealed a melting endotherm at 107°C and a reaction exotherm at 331°C with an onset temperature of 290°C. The glassy product which resulted appeared to be polymeric and complex.

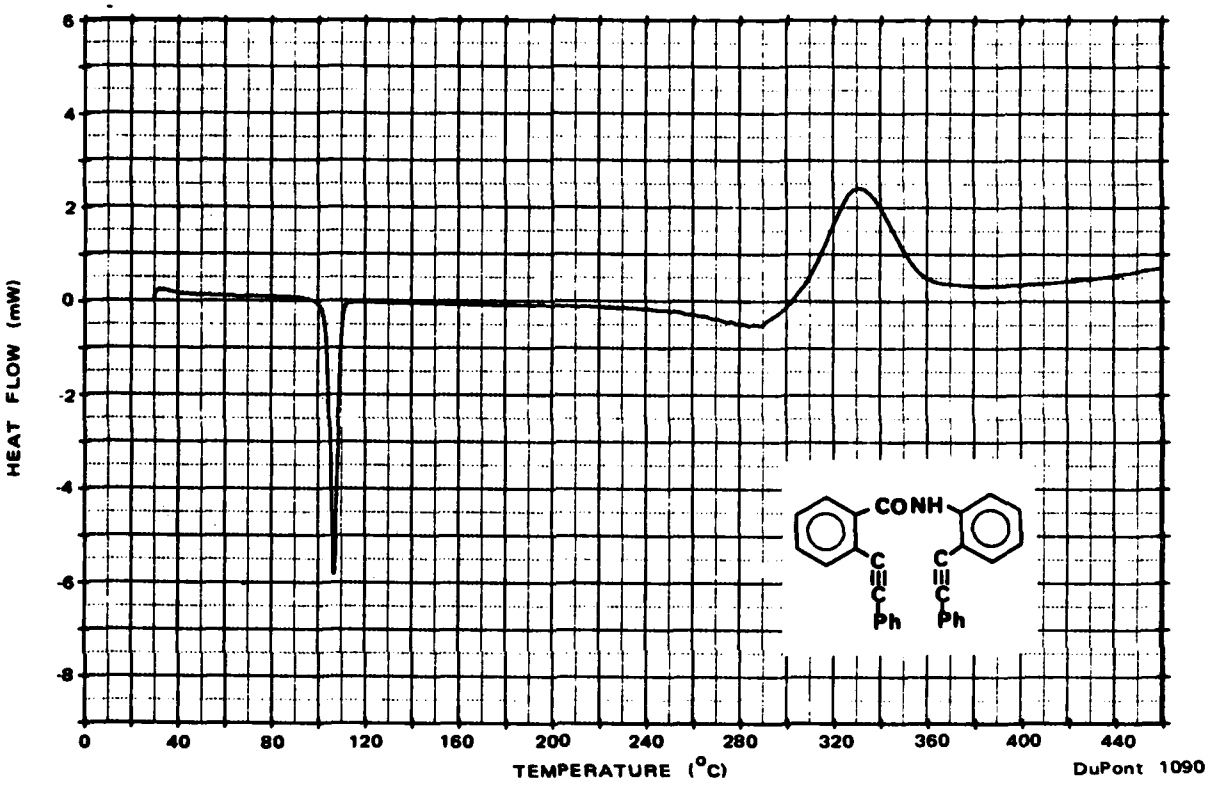
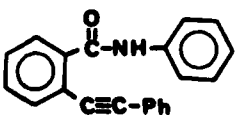
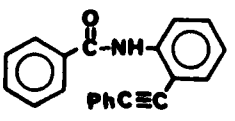


Figure 2. Differential Scanning Calorimetric Thermogram of Compound 85.

By the removal of one of the two phenylethynyl substituents from structure 85, two isomeric compounds 87 and 69 would result. The thermal behavior of compound 87 has been

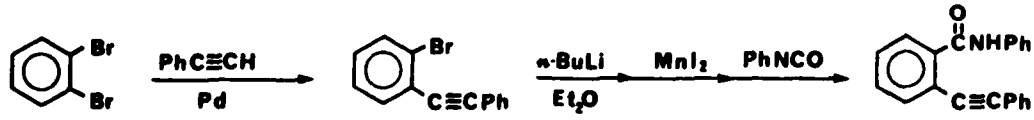


(87)



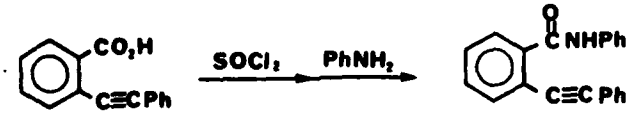
(69)

the subject of a related study (Reference 139). The synthesis of N-phenyl-2-(phenylethynyl)-benzamide (87) was accomplished by a sequence starting from 1,2-dibromobenzene (88).



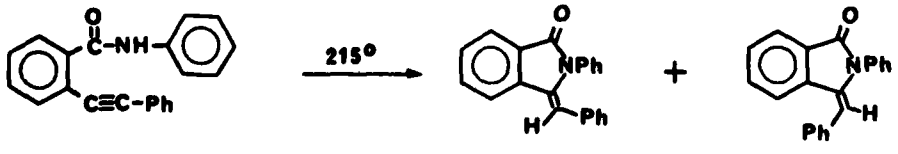
(88) (87)

Based on results from our laboratories, an alternate synthesis would be possible from 2-(phenylethynyl)benzoic acid (78).



(78) (87)

Compound 87 exhibited a reaction exotherm maximum at 232°C on its DSC curve. When heated at 215°C, 87 gave an isomeric mixture of 89 and 90.



(87) (89) (90)

Compound 69 was synthesized by palladium-catalyzed phenylethynylation of N-(2-iodophenyl)benzamide (vide supra). The differential scanning calorimetric (DSC) data showed a melting endotherm minimum at 118°C and a broad reaction endotherm minimum at 290°C. The broad reaction endotherm at 290°C was unexpected, since the ortho-iodo analog of 69 exhibited an exotherm above 280°C (Figures 3, 4).

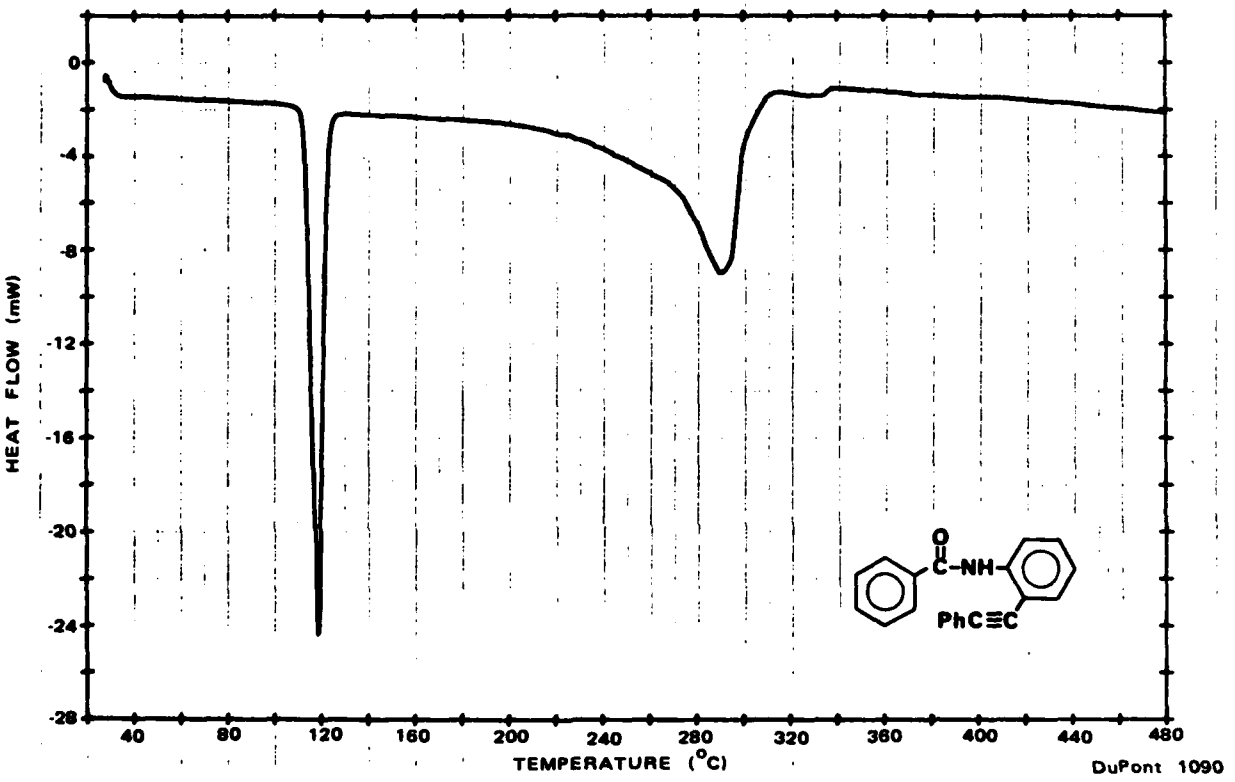


Figure 3. Differential Scanning Calorimetric Thermogram of Compound 69.

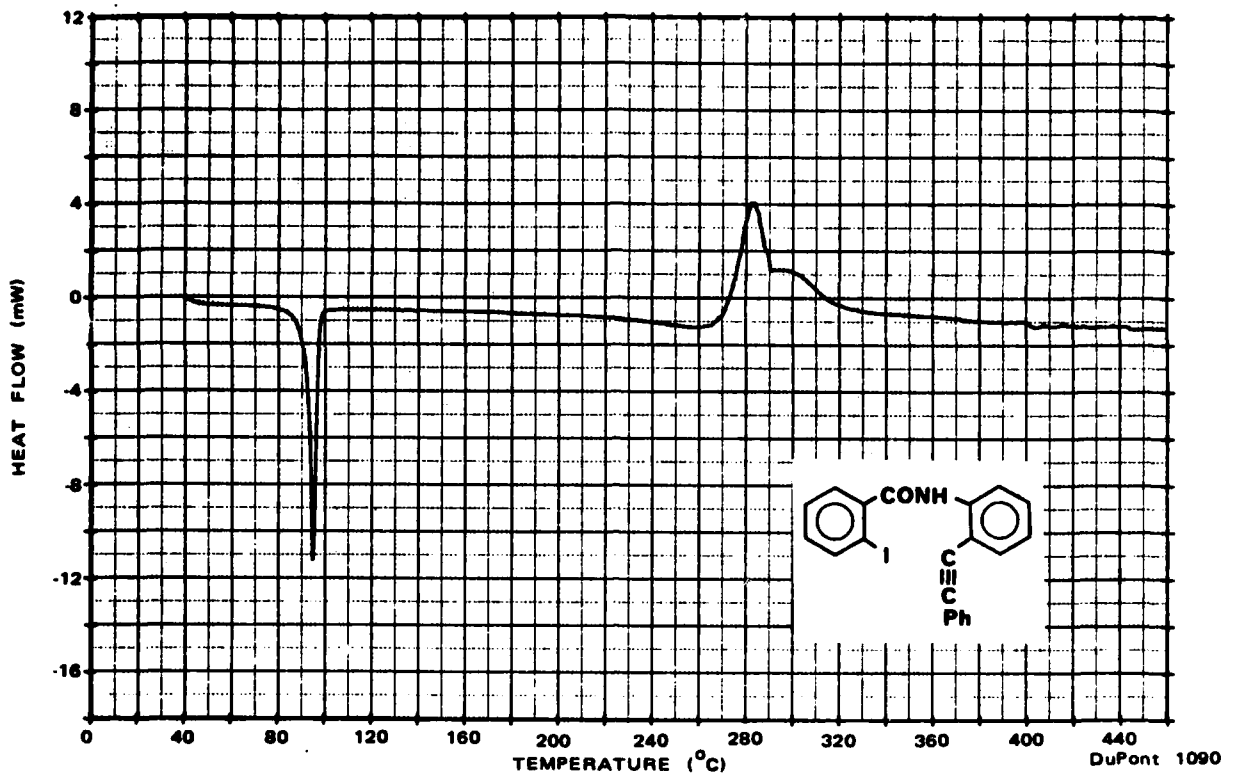
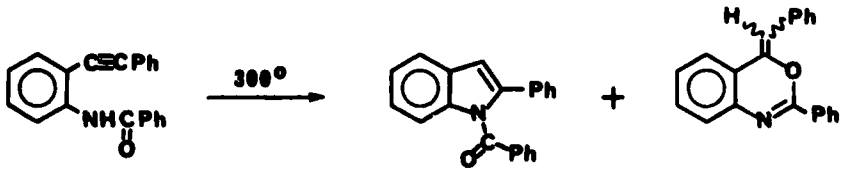


Figure 4. Differential Scanning Calorimetric Thermogram of Iodo-Analog of 69.

At 300°C under an inert atmosphere, compound 69 underwent a rearrangement reaction to yield two structural isomers 91 and 92 which were separable by careful column chromatography. Structure elucidation was accomplished by IR, MS, NMR and elemental analysis. The overall isolated yield of 91 and 92 was high. Mechanistically, 91 arises from nucleophilic



(69) (91) (92)

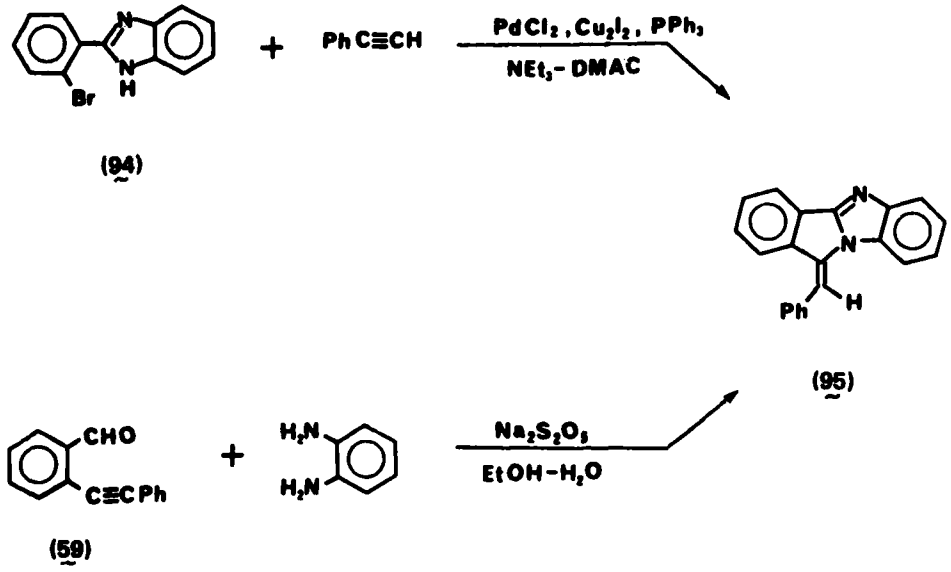
addition of the nitrogen-hydrogen bond to the proximal ethynyl bond and 92 arises from attack of the oxygen center of the tautomeric enaminol form of 69. This intramolecular cyclization (IMC) reaction is novel but the difference in melting points between 69 and either 91 and 92 is not large enough to render itself useful to the design of IMC reactive polymers.

2-(2-Phenylethynyl)phenylbenzimidazole (93) is structurally a potential candidate for intramolecular cyclization. Our first approach to its synthesis used 2-(2-bromophenyl)benzimidazole (94) as starting material, which derived from 2-bromobenzaldehyde bisulfite adduct and o-phenylenediamine (Reference 140).

(94) (93)

The phenylethynylation of 94 appeared to be inefficient and also sensitive to the nature of the palladium catalyst used. In the presence of palladium acetate, no phenylethynylation took place as 94 and phenylacetylene were heated either in 1:1 toluene-triethylamine at reflux for 12 hr. or in 1:1 N,N-dimethylacetamide(DMAC)-triethylamine at 80°C for 24 hr. In the presence of the $Ph_3P/(Ph_3P)_2PdCl_2/Cu_2I_2$ catalyst system in 1:3 DMAC-triethylamine at 90°C for 36 hr. (Reference 27), an incomplete reaction took place. The NMR spectrum taken in DMSO-d_6 of the product mixture after work-up showed an overwhelming presence of starting material 94 (67%) and absorptions due to a novel product (33%). The reaction product was isolated by silica gel column chromatography, eluting with dichloromethane.

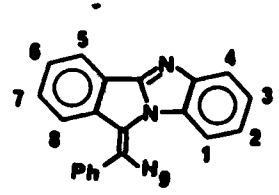
Structure elucidation for this product was carried out in conjunction with the reaction product isolated from the reaction between 2-(phenylethynyl)benzaldehyde (59) bisulfite adduct and o-phenylenediamine. Both reaction products appeared to be the same compound 95, since all their spectra (NMR, IR and MS) were identical when superimposed on each other. Compound 95 is an isomer of the desired phenylethynylated product 93. Structural assignment for 95 was based on available physical data and elemental analysis.

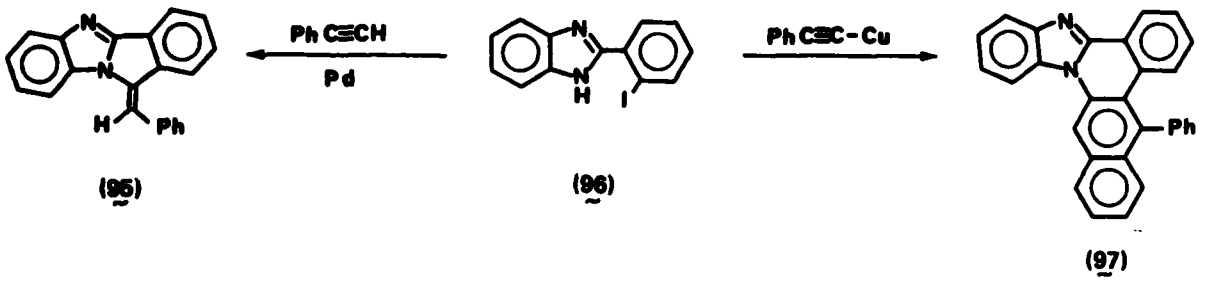


Unambiguous assignment of NMR chemical shifts to the respective protons was made on the basis of double resonance experiments (Table 3).

The isolation of 11-benzylidene-1H-isoindolo[2,1a]benzimidazole (95) from the palladium-catalyzed phenylethynylation reaction of 2-(2-bromophenyl)benzimidazole (94) was interesting in light of previous work at the AFWAL Polymer Branch. It was found that palladium-catalyzed phenylethynylation of 2-(2-iodophenyl)benzimidazole (96) was also incomplete and afforded a solid compound which exhibited no reaction exotherm on its DSC curve. We established that this solid compound was identical to 95. The 250-MHz PMR and mass spectra were identical when superimposed on those obtained for 95. In the reaction of 2-(2-iodophenyl)benzimidazole (96) with copper[I] phenylacetylide, however, a different compound, based on thin-layer chromatography, was obtained. This compound also yielded no DSC reaction exotherm below 300°C but a sharp endotherm due to melting was observed at 324°C (Figure 5). The mass spectrum indicated a molecular ion of m/e 392 (or 394) and a base peak at m/e 243. Fourier-transform infrared spectroscopy showed no prominent absorptions. A tentative structure 97 was assigned to this compound.

TABLE 3. 250-MHz PMR CHEMICAL SHIFT ASSIGNMENT OF 11-BENZYLIDENE-1H-ISOINDOLO[2,1a]BENZIMIDAZOLE

	H_1	$H_{2,3,4}$	H_5	H_6	H_7	H_8	H_9	H's on pendent phenyl
δ	8.89–8.92	7.68–7.74	7.99, 8.02	7.41	7.02	6.49, 6.52	6.92	7.62
Multiplicity	m	m	dxt $J_{5,6} = 8.2$ $J_{5,7} = 1.0$	dxdxd $J_{6,5} = 8.3$ $J_{6,7} = 7.5$ $J_{6,8} = 1.0$	dxdxd $J_{7,5} = 1.0$ $J_{7,6} = 7.5$ $J_{7,8} = 8.3$	dxt $J_{8,6} = 1.0$ $J_{8,7} = 8.3$	broad s	m



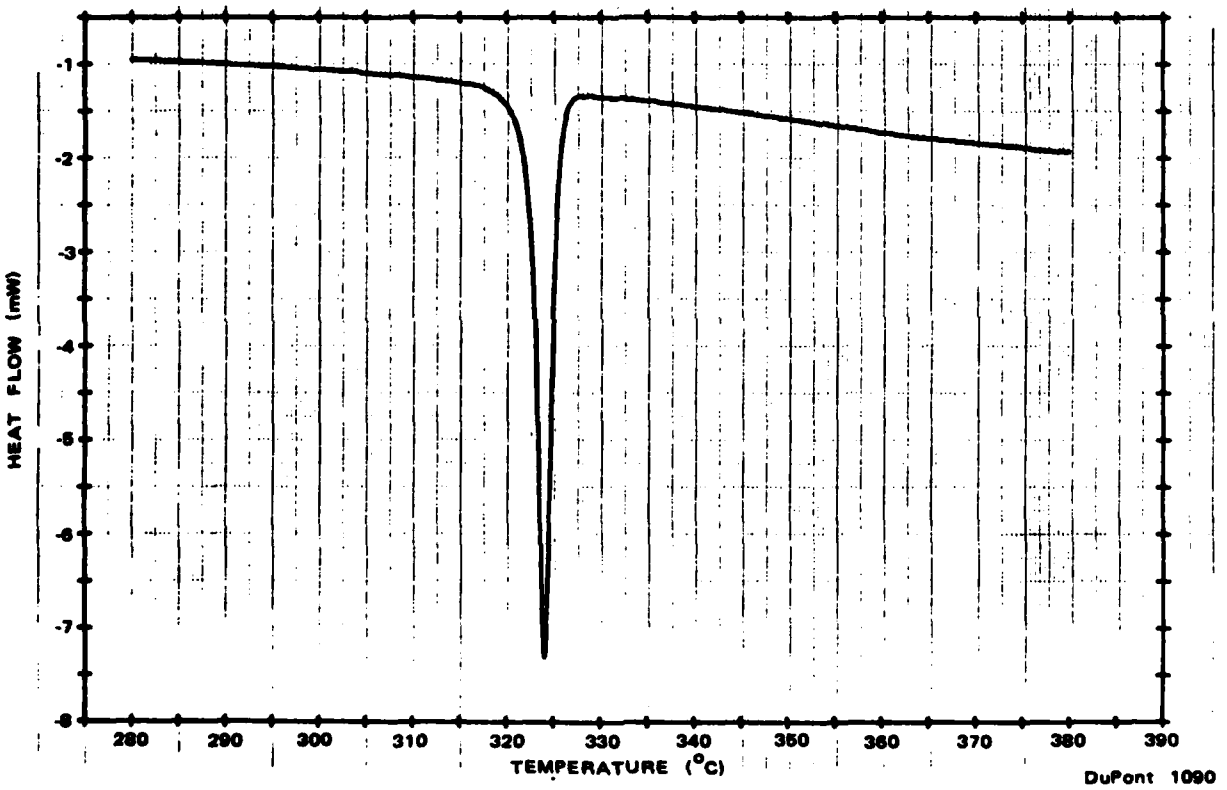
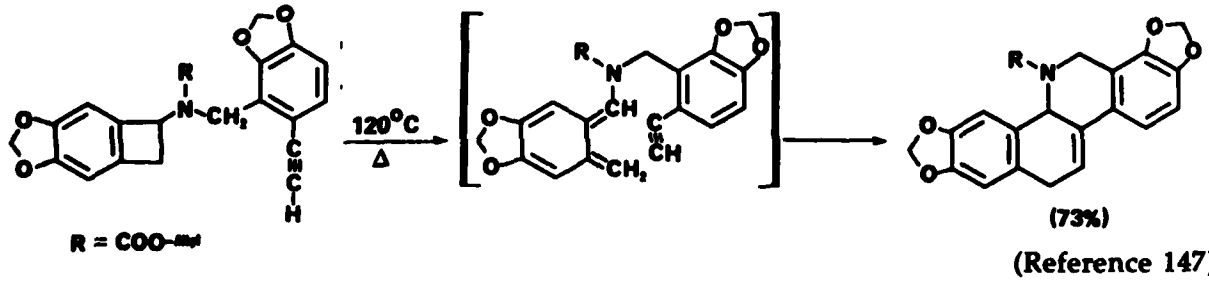


Figure 5. Differential Scanning Calorimetric Thermogram of Compound 97.

Intramolecular Diels-Alder Reactions

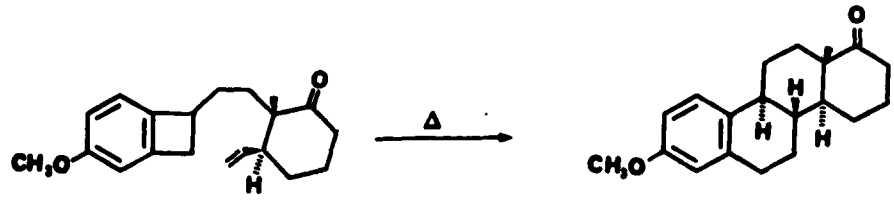
Bimolecular Diels-Alder reactions are characterized by a highly-ordered aromatic transition state (Reference 141). Recent investigations have produced ample examples of Diels-Alder reactions occurring intramolecularly when both diene and the dienophile are predisposed in the same molecule. The principle of intramolecularity greatly increases the synthetic potential of these reactions. For example, dienophiles, such as isolated carbon-carbon and carbon-nitrogen double and triple bonds, which are normally unreactive in the classical Diels-Alder fashion, become reactive to the diene bound on the same molecule. This is presumably due to entropic assistance as a result of the close proximity of the reaction partners. Three important reviews on intramolecular Diels-Alder reactions have appeared (References 142, 143, 144).

Our interest in the benzocyclobutenes (Reference 145) was prompted by the intramolecular Diels-Alder addition reaction of ethylenes and acetylenes with o-quinodimethanes, of which benzocyclobutenes are precursors (References 142, 143, 144, 146). The thermal generation of the highly reactive o-quinodimethanes (and their subsequent Diels-Alder reactions) has provided an elegant entry to the synthesis of a variety of natural products which are difficult to synthesize otherwise. The high stereoselectivity is remarkable (References 147, 148, 149, 150, 151).

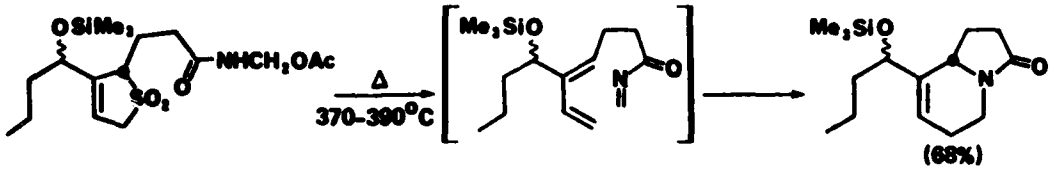


R = COO-

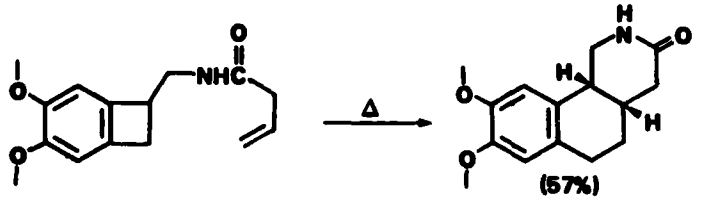
(Reference 147)



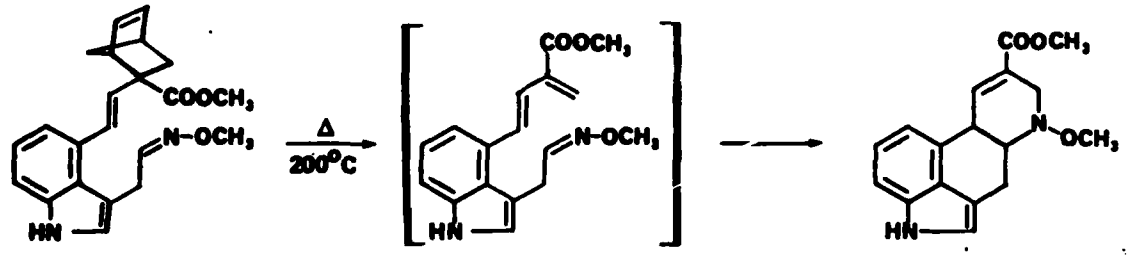
(Reference 148)



(Reference 149)

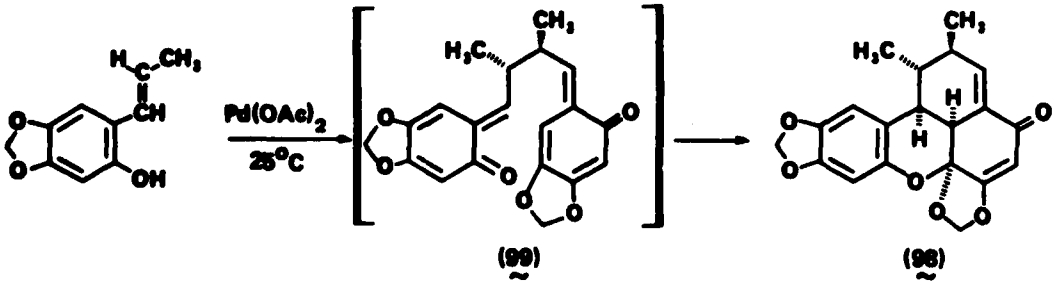


(Reference 150)



(Reference 151)

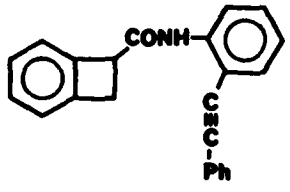
In a very similar approach whereby the lignan carpanone (98) was synthesized via an intermediate bis-o-quinodimethide (99) (i.e., the oxygen analogue of o-quinodimethane), the stereochemical control over five chiral centers is striking (Reference 152).



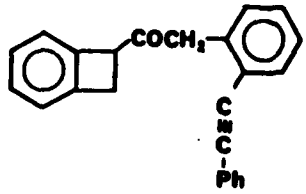
(99) (98)

Benzocyclobutenyl Systems

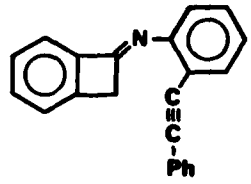
The intramolecular Diels-Alder addition of o-quinodimethane to acetylene sparks new promise to our search for a novel IMC cure mechanism. The following benzocyclobutenyl systems show great potential.



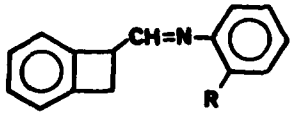
(100)



(101)

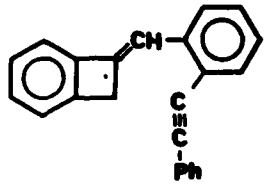


(102)

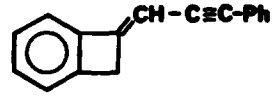


(103) R= H

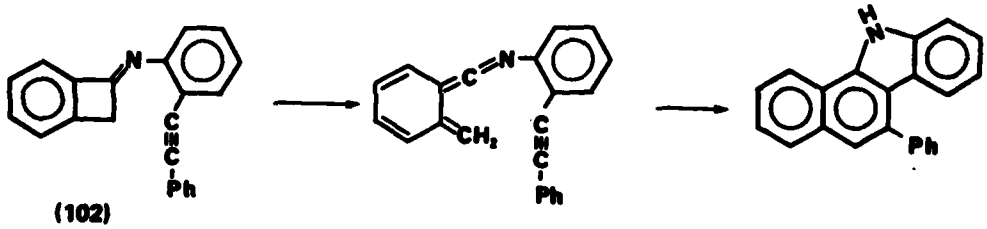
(104) R= PhC≡C-



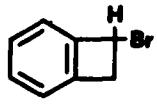
(105)



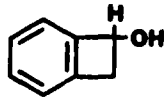
(106)



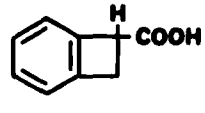
(102)



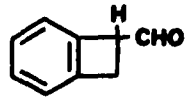
(107)



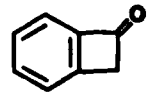
(108)



(109)



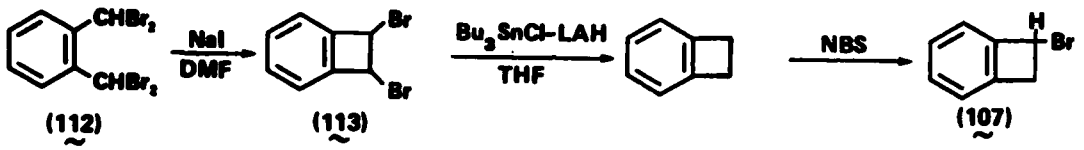
(110)



(111)

Synthesis of the requisite benzocyclobutene precursors, i.e., 107–111, was carried out. We commenced our pursuit of 1-bromobenzocyclobutene (107) with commercially available α,α,α′,α′-tetrabromo-o-xylene (112), which underwent a ring closure reaction in the presence of sodium iodide to yield a mixture of cis- and trans-1,2-dibromobenzocyclobutene (113) (References 153, 154). The isomers were used together in the subsequent reduction to benzocyclobutene with tri-n-butyltin hydride formed in situ from tri-n-butyltin chloride and lithium aluminum hydride (Reference 155). Benzylic bromination with N-bromosuccinimide in the presence of a free-radical initiator converted benzocyclobutene to 1-bromobenzocyclobutene (Reference 153).

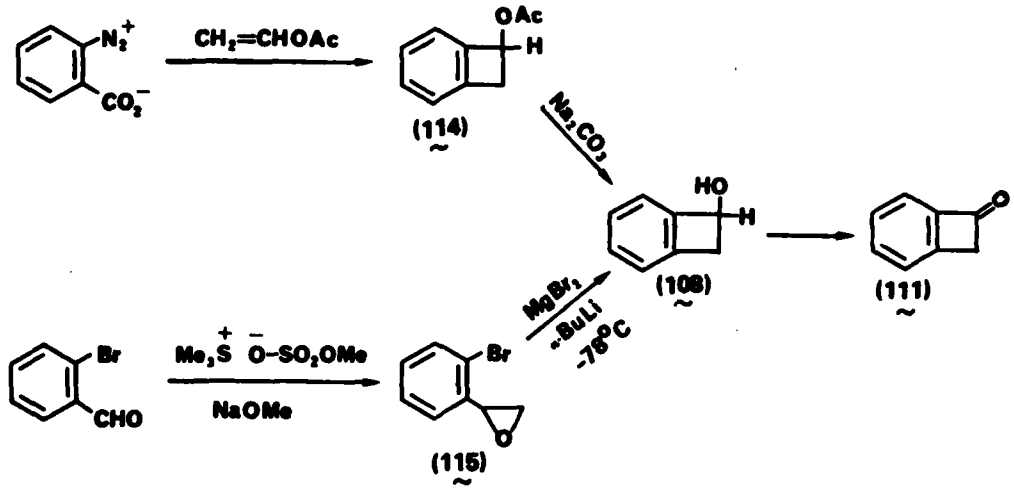
Scheme 11



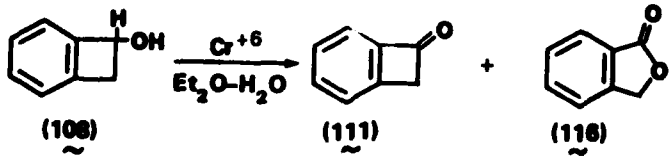
(112) (113) (107)

There were two approaches which we undertook to prepare benzocyclobutenol (108) for the subsequent conversion to benzocyclobutenone (111) (Scheme 12). The classical approach is by way of the benzyne addition to vinyl acetate (Reference 156) and subsequent deacetylation of the adduct 114. The prior synthesis of the diazonium salt (Reference 157) for the generation of benzyne is a hazardous procedure for scale-up operations. We therefore preferred an experimental procedure that allows the in situ generation of the diazonium salt in low concentration (Reference 158). At the end, 1-acetoxybenzocyclobutene (114) was prepared in 43.5% yield. Removal of the acetyl group by sodium carbonate yielded benzocylobutenol (108) (References 156, 158, 159). In a comparative study, 2-bromostyrene oxide (115) was prepared by a newly-reported dimethyl sulfate-dimethyl sulfide method (Reference 160). A ring opening reaction of 115 by the action of n-butyllithium and magnesium bromide afforded benzocyclobutenol (108) (References 161, 162).

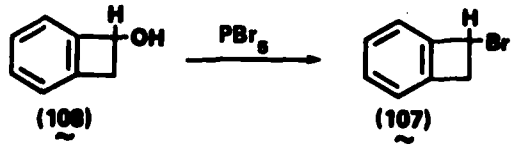
Scheme 12



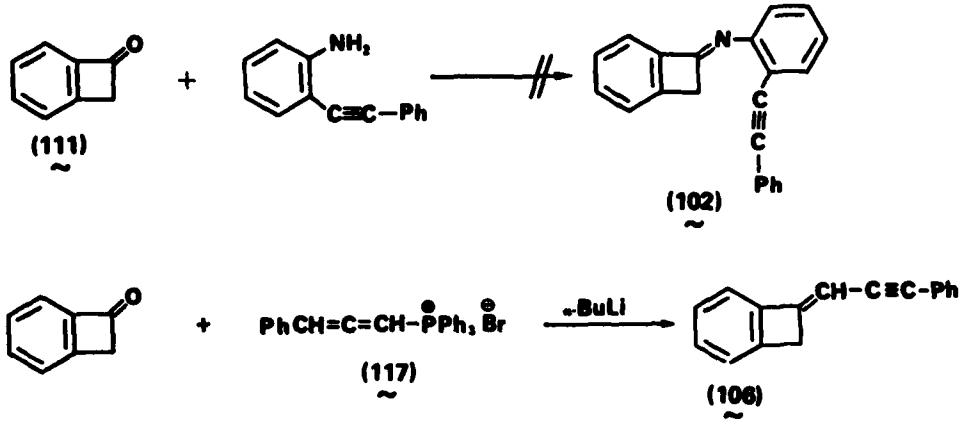
In earlier literature reports, the oxidation of 108 was carried out using chromic anhydride in pyridine (42% yield) (Reference 163), or activated manganese dioxide (90% yield) (Reference 159). We found that 108 was easily oxidized to benzocyclobutenone by a convenient method using diethyl ether and aqueous chromic acid (Reference 164). The desired benzocyclobutenone (111) was cleanly separated from the accompanying minor product, phthalide (116).



The ready availability of benzocyclobutenol (108) (Scheme 12) makes it a convenient precursor to both 1-bromobenzocyclobutene (107) and benzocyclobutenone (111). We therefore examined the conversion of 108 to 107 using phosphorus pentabromide. The transformation was essentially quantitative.



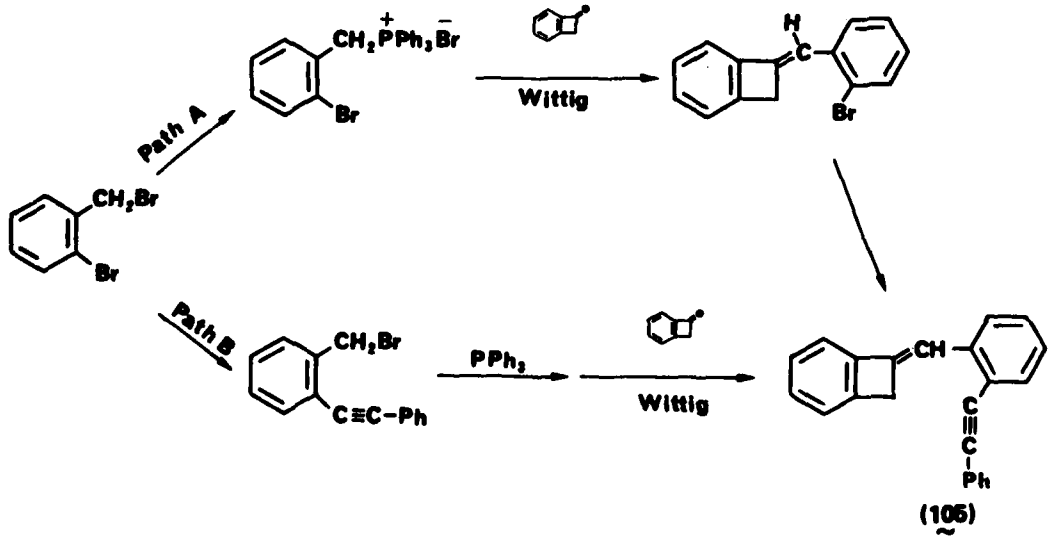
The synthesis of Compound 102 was not accomplished through direct imine formation between benzocyclobutenone (111) and 2-aminotolane (References 28, 165). Compound 106 (as an E and Z mixture) was obtained from 117 via a Wittig reaction. It is relevant to point out that the allenic phosphonium salt (117) was prepared from phenylpropargyl bromide and triphenylphosphine. The allenic structure was ascertained by IR spectroscopy. Upon treatment of 117 with n-butyllithium, the propargyl form was regenerated in the ylid (Reference 166).



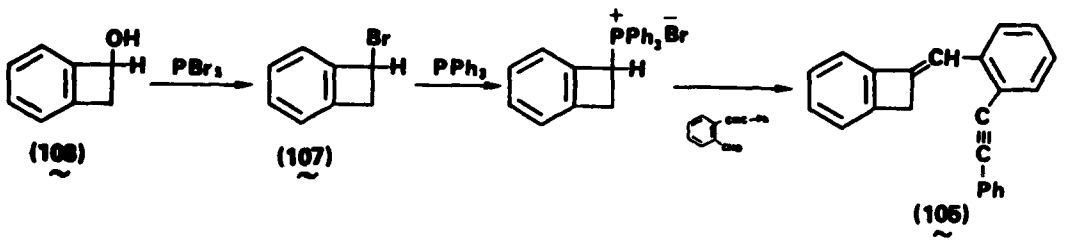
Compound 105 could conceivably be attained in several ways (Scheme 13). The benzocyclobutenone route (Procedure I) was briefly examined, but was quickly abandoned in light of a more convenient approach via the bromobenzocyclobutene route (Procedure II).

Scheme 13

Procedure I:

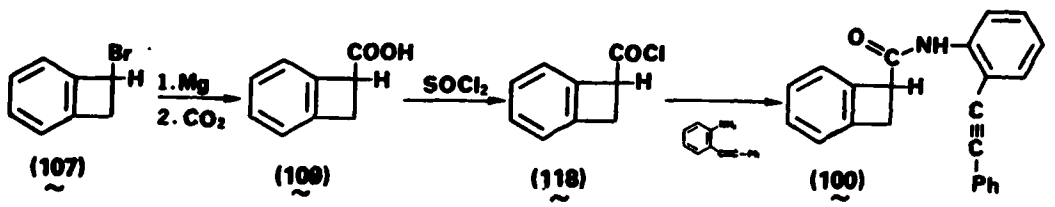


Procedure II:

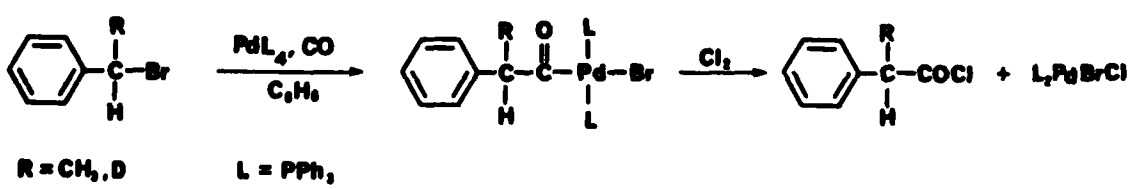


Compound 100 was synthesized from bromobenzocyclobutene (107) via the sequence depicted in Scheme 14. The Grignard compound made from 107 was carbonated to yield the acid 109 (Reference 167) which was then converted to its acid chloride 118 (Reference 168). Treatment of 118 with 2-aminotolane gave the target compound 100. It was later demonstrated that the synthesis of Compound 100 could be effected smoothly in one pot from the carboxylic acid intermediate (109).

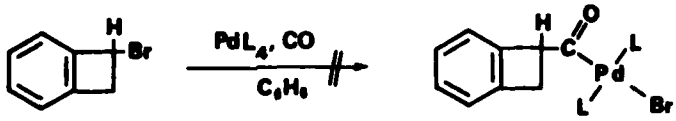
Scheme 14



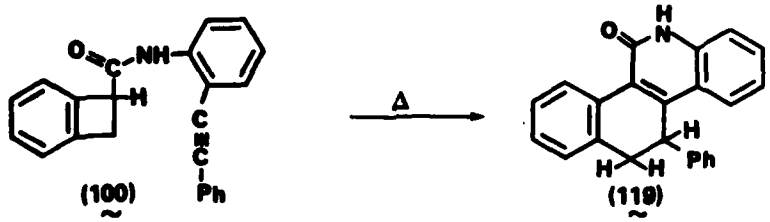
The conversion of the benzylic bromide 107 to 100 through the carboxylic acid chloride 118 suggests a plausible application of an organopalladium method, which would allow a one-pot synthesis of 107 → 100 under mild conditions. Tetrakis(triphenylphosphine)-palladium[0] (Reference 108) is known to undergo an oxidative addition-carbonylation reaction with benzyl bromides in the presence of carbon monoxide to yield the corresponding acylpalladium[II] complexes, which react with gaseous chlorine to give the acyl chlorides and bromochlorobis(triphenylphosphine)palladium[II] (Reference 169).



It is reasonable to expect 1-bromobenzocyclobutene (107) to undergo an analogous sequence to yield 118 which should require no isolation and would react with 2-aminotolane to give 100. Unfortunately, 1-bromobenzocyclobutene failed to undergo oxidative addition with tetrakis(triphenylphosphine)palladium[0].



Compounds 105 and 106, by differential scanning calorimetry (DSC), did not give any appreciable exotherm below 250°C (Figure 6). Upon heating at 225° ± 5°C for several hours, the starting materials were isolated. In contrast, Compound 100 gave a melting endotherm at 108°C and an exotherm at 225°C (Figure 6). At 225°C, Compound 100 rapidly underwent a reaction. Thin layer chromatography indicated that the reaction was fairly clean and was over in less than 2 hours. The reaction product was isolated by column chromatography. It remained a white solid up to 240°C and gradually turned yellow. Near 300°C it turned brown and did not melt even at 315°C. Mass spectrometric analysis indicated that this material was isomeric to the starting material. The available physical data allow a tentative assignment of structure 119 to the product.



(100) (119)

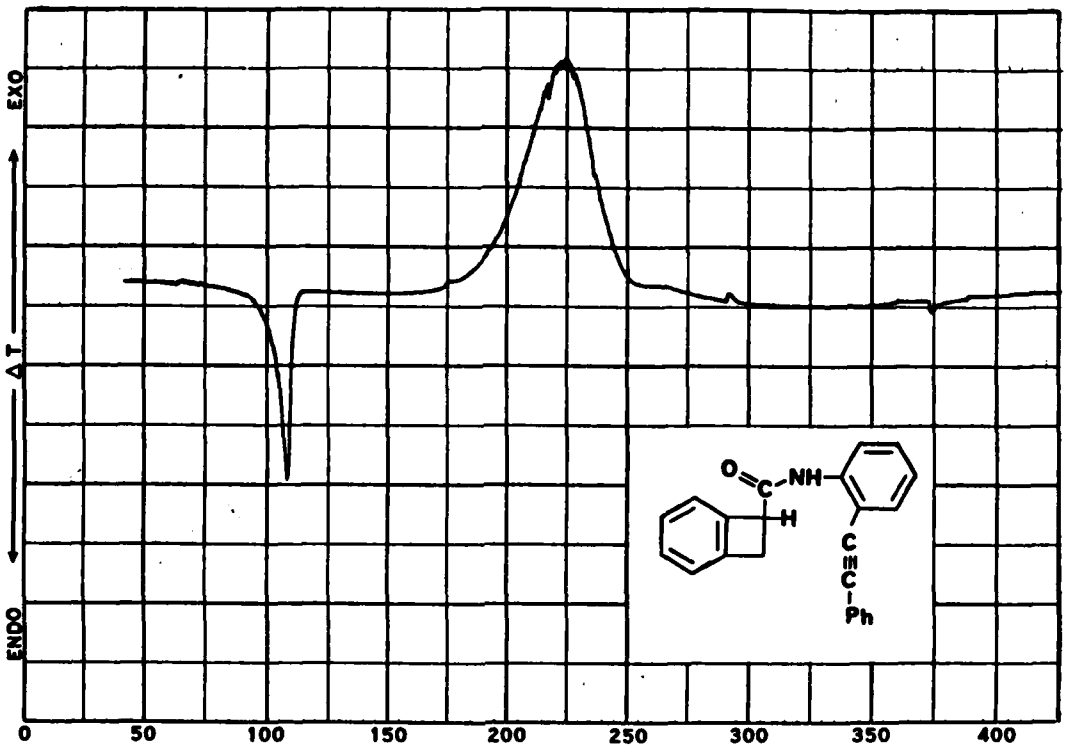
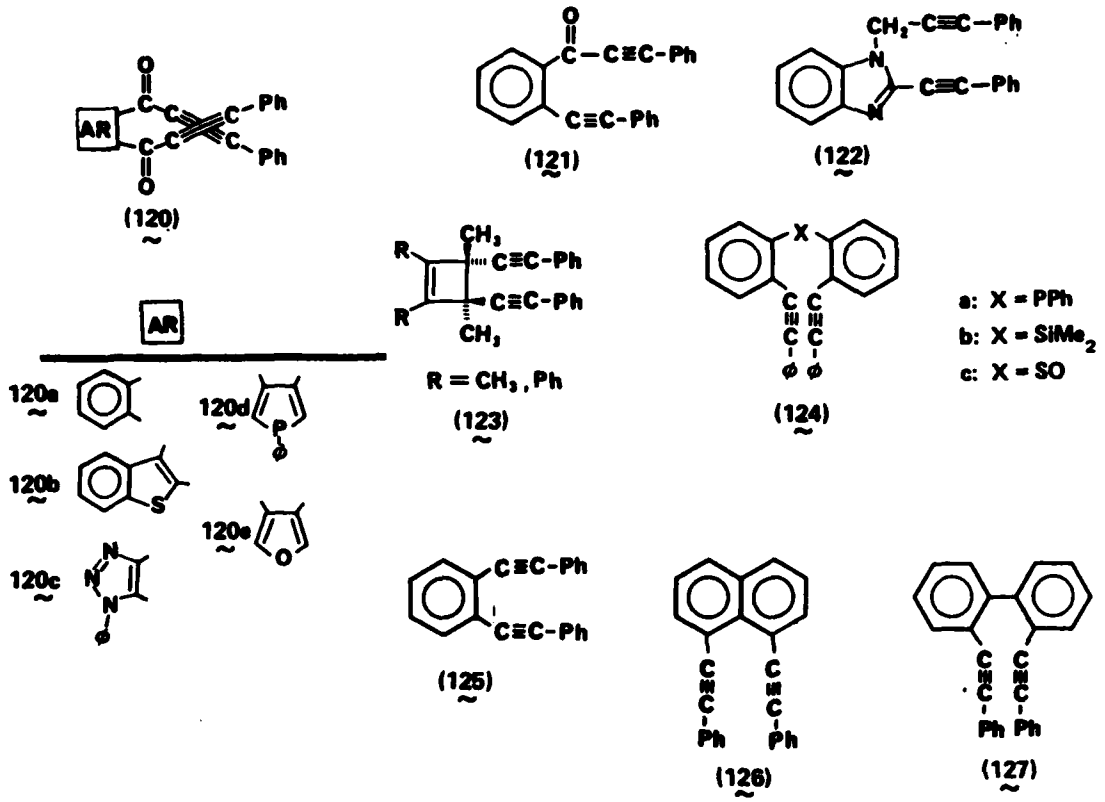


Figure 6. DSC Thermogram of Compound 100

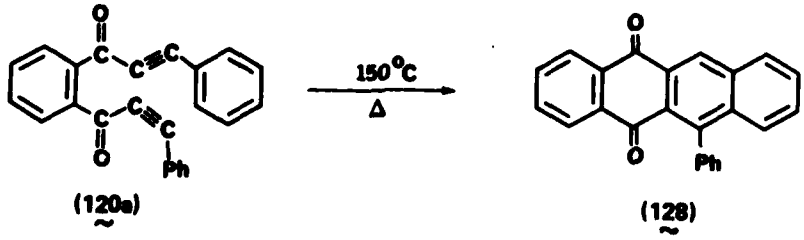
Ortho-Bis(phenylethynyl) Compounds

Extensive research has been carried out on the synthesis and chemical behavior of compounds having ortho-positioned phenylethynyl pendants. Structurally, these compounds can be categorized into four classes: the aromatic and heteroaromatic keto-diynes (120, 121, 122), the cyclobutene-trans-diynes (123), bis-tolane derivatives of phosphorus, silicon and sulfur (124) and the bis(phenylethynyl) aromatics (125, 126, 127). Compound 127 is the state-of-the-art thermally active IMC system.



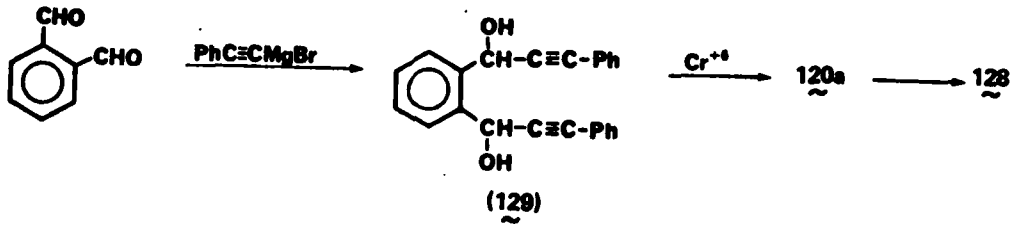
The photochemical and organometallic chemistry of these classes of compounds have been reviewed (Reference 123). Only sporadic data on the thermal reactions are available. In the case of the bis(phenylethynyl) compound 120a, its organorhodium (References 170, 171) and organonickel chemistry yielded interesting results (Reference 172).

It is significant to note that the fused aromatic system 128 was isolated in 1% yield from a benzene solution of 120a after prolonged standing at room temperature. The possibility of a thermally induced intramolecular cyclization of 120a was later realized (Reference 173).

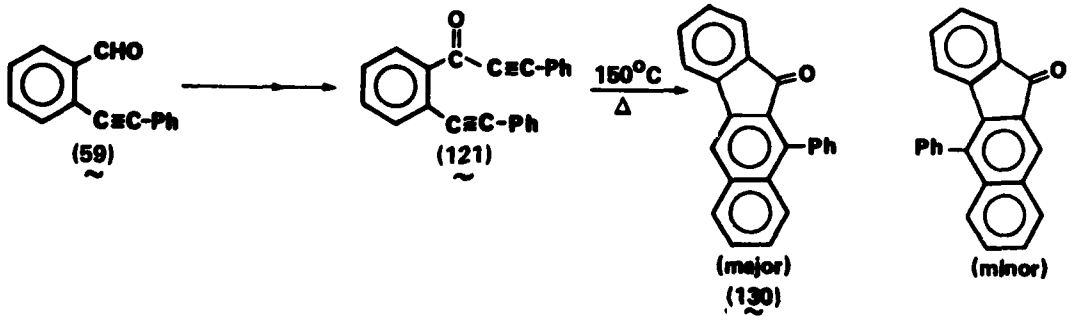


An analogous thermal reaction also took place in the case of o-bis-(phenylpropargyl)benzene. Irradiation of 120a similarly gives 128. The mechanism proposed for the photochemical reaction involves an initial formation of the reactive cyclobutadiene by a [2+2] cycloaddition, followed by ring cleavage to the diradical which undergoes rearrangement and then recombination, while the thermal reaction is likely to follow a concerted [2+2+2] mechanism.

The thermal reaction of 120a is intriguing, especially the enhancement in the melting point going from starting material 120a (mp 94-95°C) to product 128 (mp 284°C). We briefly evaluated the synthesis of 120a and its potential as a candidate thermal IMC system. Treatment of o-phthalaldehyde with two equivalents of (phenylethynyl)magnesium bromide afforded the intermediate diol 129 (Reference 174). A conventional manganese dioxide oxidation for this type of compound was not followed in light of a far easier oxidation procedure (Reference 164) using aqueous chromic acid and ether. Our preliminary experiment yielded an orange-yellow powdery product which showed physical characteristics of 128 instead of the expected 120a. Further experimentation is needed to decide whether the premature thermal ring closure took place during the oxidation process or in subsequent work-up.

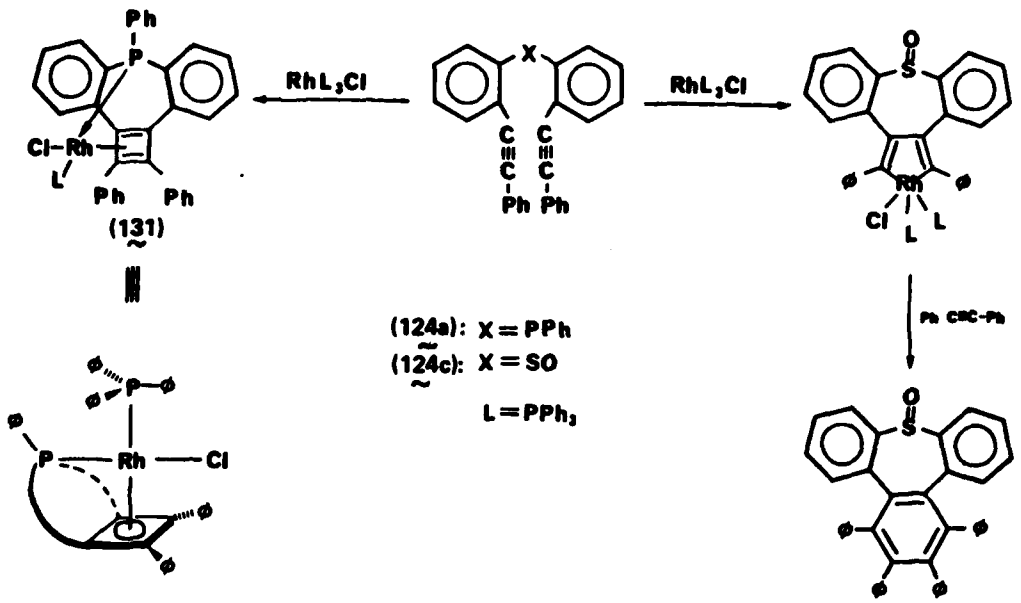


The availability of 2-(phenylethynyl)benzaldehyde (59) prompted us to synthesize compound 121 which is structurally similar to 120a. The Grignard reaction of 59 and subsequent oxidation of the intermediary alcohol derivative presented no complications. The oily compound 121 (Reference 175) underwent a reaction at 150°C to yield 10-phenyl-11H-benzo [b]fluoren-11-one (130), its 5-phenyl isomer being present as a minor product. Identification of products was possible by comparison of their physical and spectral characteristics with literature values (Reference 176).

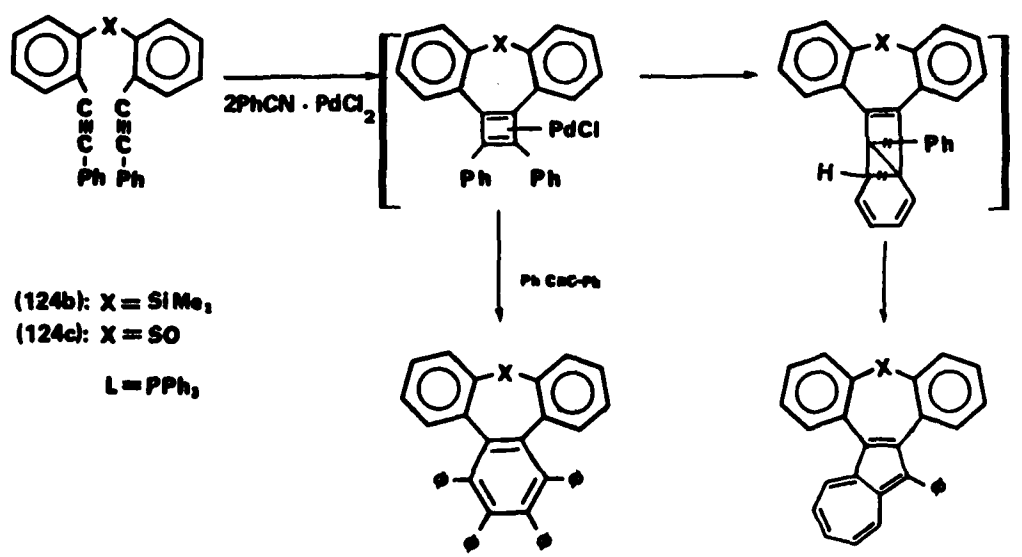


Bis-tolane derivatives of phosphorus, silicon and sulfur (124) are interesting in their resemblance to 2,2'-bis(phenylethynyl)biphenyl, having criss-crossing phenylethynyl substituents. While the organorhodium chemistry of the sulfur compound 124c (Reference 177)

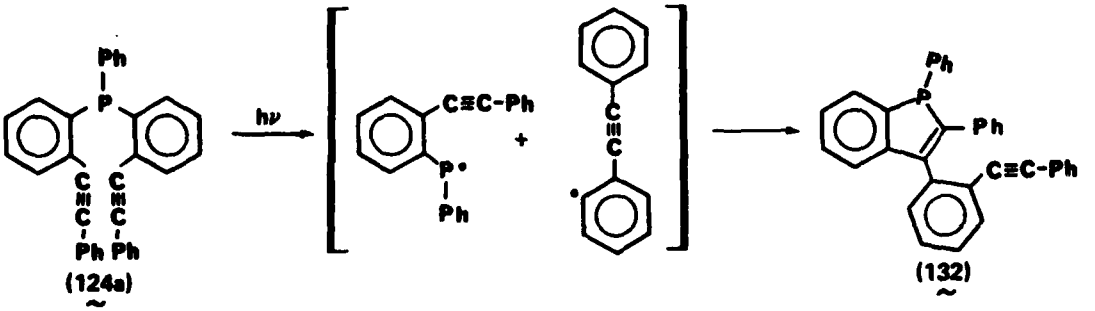
parallels that of keto-diynes 120, the phosphorus analog 124a undergoes complexation with chlorotris(triphenylphosphine)rhodium[I] to yield a novel cyclobutadiene-rhodium[I] complex 131 (Reference 178).



Both 124b (Reference 179) and 124c (Reference 177) yield substituted azulenes in the presence of an organopalladium complex. The structure of the cyclobutadiene-palladium complex initially formed during the reaction is inferred both from the trapping experiment with diphenylacetylene and azulene formation.



Thermal cyclization studies of 124 have not been reported. An interesting rearrangement-cyclization reaction (Reference 180) of 124a occurs upon irradiation, however. The structure of the photochemical product 132 has been established by an X-ray study of its methyl iodide salt.



It is expected that the presence of heteroatoms such as phosphorus, silicon and sulfur in high temperature resistant polymer resins can contribute to their flexibility and flame retarding ability without adversely affecting their requirement of thermal stability. The criss-cross disposition of the two pendent phenylethynyl groups sets the stage for a possible thermally-induced intramolecular cycloaddition akin to the state-of-the-art 2,2'-bis(phenyl-ethynyl)biphenyl IMC system. Future research in this direction may prove to be a successful undertaking.

3. TASK III. CHEMISTRY AND APPLICATION OF ISOIMIDE REARRANGEMENT

The development of the intramolecular cyclization (IMC) cure method effectively eliminates the restriction of translational molecular mobility generally needed for crosslinking cure. Thus, the thermal cure step, which causes pairs of strategically positioned pendent groups along the polymer chain to undergo an intramolecular cycloaddition to form a fused aromatic structure, can continue to completion long after the resin is essentially vitrified. The ultimate use temperature would be substantially higher than the cure temperature. The intramolecular nature of the curing process precludes the formation of a three-dimensional structure. Since the reaction used for the curing process is of the cycloaddition type, no volatiles are evolved. As presented in earlier sections, the thermal cycloaddition reaction of 2,2'-bis-(phenylethynyl)biphenyl (References 11, 12) has been successfully adopted for curing quinoxaline and imide polymers (References 14–16).

The concept of intramolecular cyclization (IMC) cure for the advancement of glass transition temperature (Tg) in polymer systems has thus far been demonstrated only with the thermal conversion of 2,2'-bis(phenylethynyl)biphenyl to 9-phenyldibenz[a,c] anthracene. It would be advantageous and desirable to be able to extend the IMC concept to other chemical systems. Several structural requirements for the potential IMC systems are important. First, the expected IMC reaction must be thermally induced and should not liberate gaseous by-products. Second, the end product of the thermal IMC reaction should be a fused aromatic or heteroaromatic ring system and/or contain trivalent nitrogens for high thermal and thermo-oxidative stability. Third, terminal phenyl rings should be present to allow functionalization. Fourth, the structural unit that undergoes the IMC reaction should be as flexible as possible so that it may contribute to the lowering of the Tg of the precure polymer, an important objective in the improvement of processibility.

Several potential IMC systems have been identified at Hughes under the sponsorship of AFWAL. However, they have not been adequately tested (vide supra).

Isoimide Technology

The recent application of isoimide chemistry to acetylene-terminated polyimide oligomer precursors (Reference 181) has brought to light the broad potential of this technology to yield easy-to-process high temperature polyimides. Especially important is the observation that the technology can be applied without compromising the thermomechanical properties of the final products. Previously, the concept of producing thermally stable addition curable polymers was severely limited by the intractability of the oligomers. Thus, monomers were selected so as to provide sufficient tractability for subsequent applications. As a consequence,

an obvious compromise had to be made between tractability at the required processing temperatures and thermal stability of the resultant products.

The introduction of isoimide functional groups into polyimide precursors drastically lowers their melting points and extends the gel time. As a result, the processing window is significantly broadened, thereby making commercially available diamines and dianhydride monomers, which previously formed intractable polyimide prepolymers, viable candidates for future resin systems. Processible polymers may now be produced with substantially increased thermal stability, relative to the state-of-the-art polyimide oligomers, e.g., HR600.

In addition to the melting point and gel time improvements, the isoimides impart to the precursors increased solubility in common low-boiling, non-interacting solvents, such as tetrahydrofuran. This is to be contrasted with state-of-the-art polyimide precursors, which generally are soluble only in strong aprotic solvents, e.g., N-methypyrrolidinone (NMP). The latter class of solvents is very difficult to remove during processing and its use often results in void formation in cured composites.

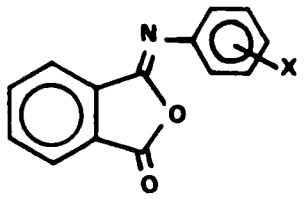
As the processibility/thermal stability dichotomy has prevented the development of ultra-thermally stable polymers ($\geq$700°F), so the toughness/thermal stability relationship has hindered widespread use of thermally stable (450–600°F) polymers.

The broadened solubility parameters of isoimides now provide a technique for introducing other polymeric moieties, which can contribute toughness and hydrolytic stability, into heretofore brittle polyimide polymer systems.

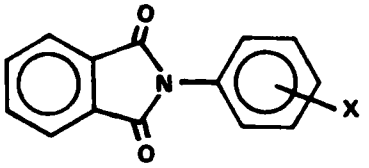
Finally, the application of this technology now provides a method for more fully exploring the structure—property relationships of polyimides, including various crosslinking techniques and mechanisms.

Chemistry of Isoimide Rearrangement

The Isoimide Technology has its basis in the findings that, under unique conditions, the chemical cyclization of polyamic acids can lead to isoimide rings which impart the added advantages to processing. The dramatic suppression in the melting range may be a consequence of the multitude of structural isomers generated in the preparation of these intermediates. The thermal rearrangement of isoimide to imide leads to no evolution of volatile byproducts, thus satisfying still another important processing requirement. In other words, processing of polyimides can now be carried out at the isoimide stage, taking full advantage of the greater solubility in common solvents, lower melting point, and longer gel time prior to the thermal which leads to the polyimides. The isoimide and imide structures are shown below:



ISOIMIDE



IMIDE

In a model study with N-substituted phthaloisoimides, a significant difference in melting point of the isoimide form over that of the imide was observed (Table 4). The dramatic decrease in melting point is very significant. Also, the solubility of the isoimide form in a number of common solvents in which the imide version is sparingly soluble is greatly increased (Reference 184).

TABLE 4. MELTING POINTS OF COMPARABLE IMIDES AND ISOIMIDES

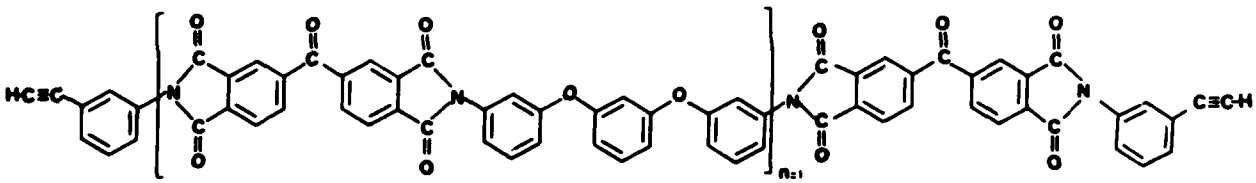
N-Substituted Phthaloisoimide	M.P.°C	
	Imide	Isoimide
C_6H_5-	207–8	110–2
o-$CH_3C_6H_4$-	180–1	135–6
p-$CH_3OC_6H_4$-	203–4	112–4
o-$CH_3OC_6H_4$-	158–9	116–7

Application of this approach to the acetylene-terminated polyimide oligomers HR600 has yielded the analogous series of acetylene-terminated polyisoimide oligomers, referred to as HR600P.

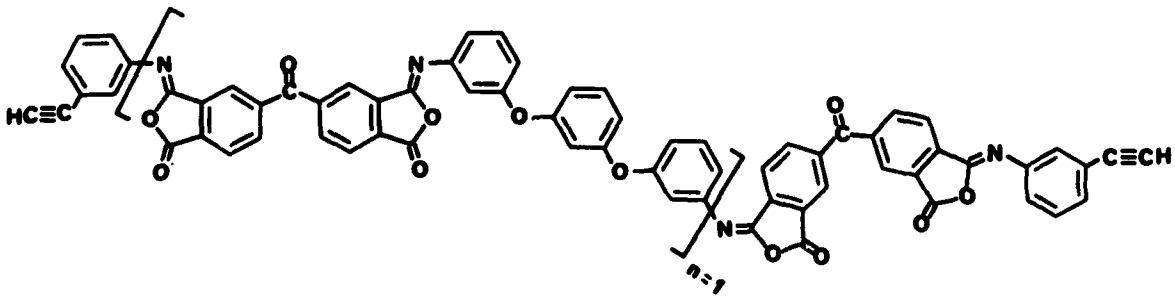
The isoimide oligomers are formed by chemical dehydration of the amic acid precursor using dehydrating agents such as N,N'-dicyclohexylcarbodiimide (DCC), ethyl chloroformate-triethylamine (TEA), trifluoroacetic anhydride (TFAA), TFAA-TEA, acetic anhydride (Reference 182), acetyl chloride and ketene (Reference 183). These dehydrating agents were screened for their application in the preparation of the HR600 resins. On the basis of their potential development into practical commercial processes the two dehydrating agents of choice were TFAA and DCC. They both promoted high conversions of the amic acid to the isoimide (Reference 185).

The structure of the acetylene-terminated isoimide (e.g., HR600P) oligomers differ from that of the corresponding imide (HR600) oligomers only in the arrangement of atoms in the functional heterocycle formed. Thus, the preparation of both oligomers requires the same stoichiometry of the reacting monomers but different reaction conditions. The HR600P oligomer melts at about 150-160°C, whereas HR600 melts at 195-205°C. Also, HR600P has excellent solubility in such solvents as tetrahydrofuran, glyme, N,N-dimethylacetamide (DMAC), N-methylprrolidinone (NMP) and other amide or ketone solvents. Upon heating and curing the HR600P converts to a thermally and oxidatively stable polymer having good physical properties.

Generally, the HR600P has an isoimide content greater than 80 percent. The theoretical structures for HR600 and HR600P are depicted in Figure 7.



HR600



HR600P

Figure 7. HR600 and HR600P

Fourier-Transform infrared (FTIR) spectroscopy provides an effective means in the analysis of polyisoimides and polyimides. The FTIR spectrum of the imide from (Figure 8) shows the expected C=O absorption frequencies (sym 1707-1730 cm^{-1}, asym 1776-1794 cm^{-1}). The FTIR spectrum of the isoimide (Figure 9) shows C=O absorption at 1789-1841 cm^{-1}, C=N absorption at 1680-1730 cm^{-1}, and a characteristic broad band base at 900-950 cm^{-1} which can be attributed to the lactone ring with an exocyclic double bond.

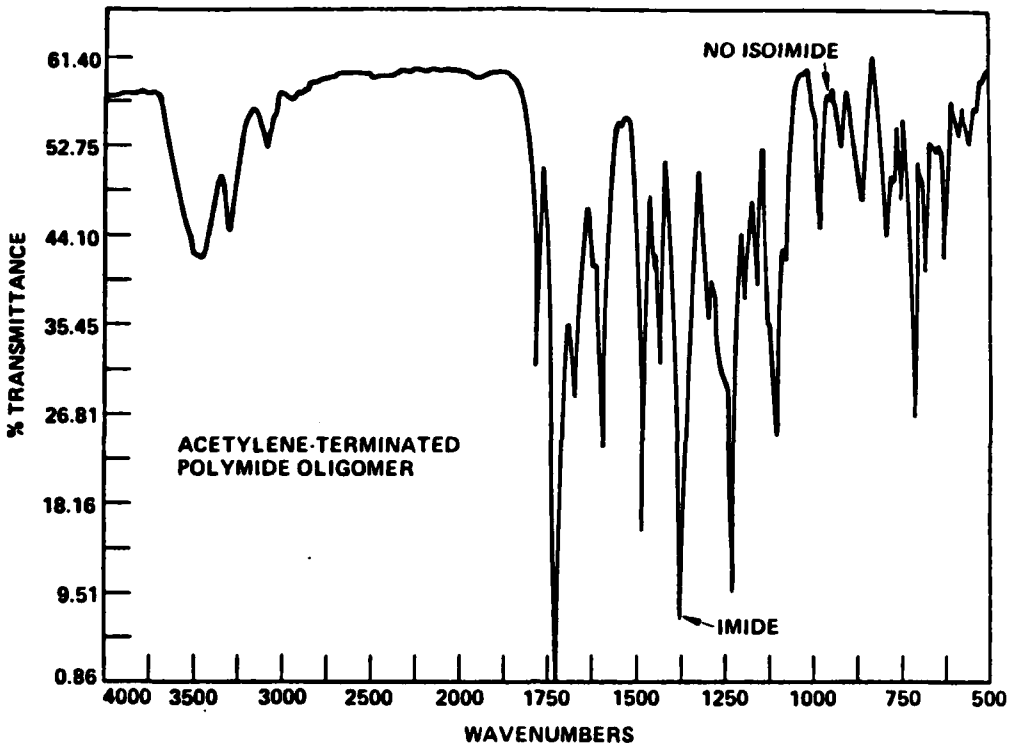


Figure 8. FTIR Spectrum of HR600 Acetylene-Terminated Polyimide Oligomer

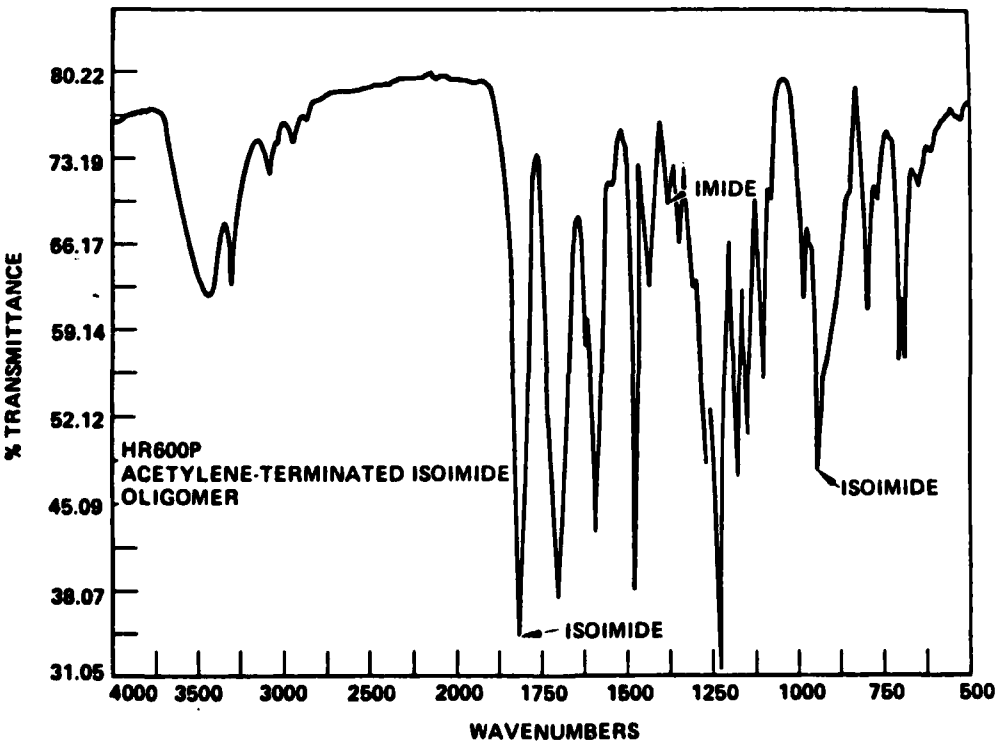


Figure 9. FTIR Spectrum of HR600P Acetylene-Terminated Isoimide Oligomer

Differential Scanning Calorimetry (DSC) of the HR600P polyisoimide oligomer shows a broader exotherm in relation to HR600. The exotherm represents a combined heat release due to the curing reaction of the acetylene end groups and also the isoimide-to-imide rearrangements. (Figure 10).

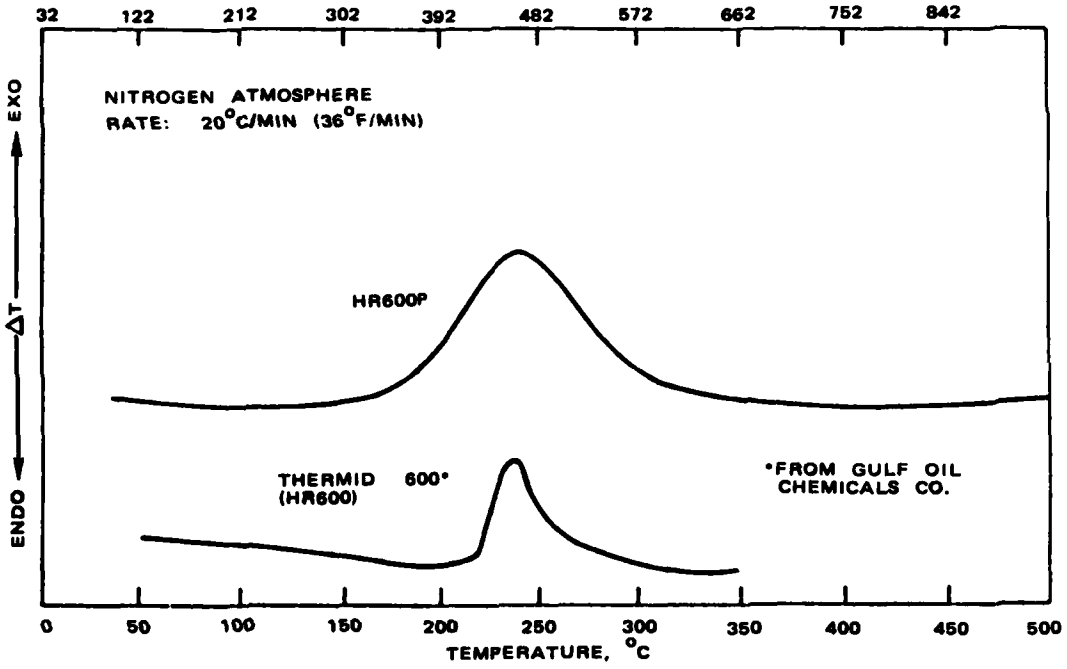


Figure 10. Differential Scanning Calorimetry Curves for HR600 and HR600P Resins

High Molecular Weight Polyisoimides

The volatile-free nature of the thermal conversion isoimide to imide and the dramatic improvements in processing characteristics observed during the development of acetylene-terminated polyisoimide oligomers jointly suggest that an alternative approach in IMC studies is possible. In order to evaluate the feasibility of using the isoimide-to-imide thermal rearrangement as the sole mechanism of processing and curing of polyimide resins, we undertook the synthesis of high molecular weight polyisoimides.

Early in the studies, techniques were established to afford monomers of polymer-grade purity. Optimization of reaction conditions was also carried out such that isoimide polymer batches having inherent viscosities (η) in the range of 0.6–1.1 could be routinely synthesized. Size exclusion chromatography of selected polyisoimides was attempted in order to correlate molecular weight averages with solution viscosity data. It seemed, however, that solution viscosity was not sensitive enough to variations in the molecular weight average and distribution. Another inherent problem in the assessment of the values of molecular weight averages was the choice of calibration standard (polystyrene).

Representative polymerization experiments are collected in Table 5. In general, polymerization was carried out in 5- to 50-gram quantities and at a concentration of 15–27% solid content. Most polyisoimide polymers obtained in this study were derived from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 4,4'-diaminodiphenyl ether (ODA), since these monomers could be obtained in a very pure form. The dianhydride 6FDA was generally obtained from the alkaline hydrolysis of the DuPont polymer NR150.

Solvent. Polyamic acid synthesis was carried out in either anhydrous N,N-dimethylaceta mide (DMAC) (Reference 186) or anhydrous tetrahydrofuran (THF). Based on inherent viscosity data, there was no significant difference observed. THF was selected for future work since it is low boiling and permits easy removal from the polymer product. Secondly, work-up is apparently simpler with a polymer solution prepared in THF solvent. Precipitation of the polyamic acid in hexane yields thin long white strings. In comparison, mixing of a polymer solution in DMAC with hexane gives a rubbery mass. In order to free occluded DMAC solvent from the polymer mass, several recycling steps (i.e., re-constitution in THF and reprecipitation of the polymer in hexane) are generally necessary.

During the period of our study, GAF Corporation was introducing a new solvent, namely, N-isopropylpyrrolidinone (NIP) which could be obtained in high purity and in the anhydrous form relatively easily. It is also infinitely miscible with hexane. Unfortunately, polymerization of 6FDA and ODA carried out in this solvent yielded a polymer of inferior quality and low inherent viscosity. Further studies in this solvent was not undertaken.

Cyclodehydration. In connection with the Hughes proprietary isoimide technology, two dehydrating agents were used in effecting cyclodehydration of polyamic acids to polyisoimides. Trifluoroacetic anhydride (TFAA) was initially employed in the synthesis of both acetylene-terminated polyisoimide oligomers and high molecular weight isoimide polymers. Outgassing experiments (Reference 181) and thermogravimetric-mass spectrometric (TGA-MS) analysis jointly suggested that TFAA had undergone reactions with the polymer to give fluorinated by-products, thus compromising the quality of the polymer. In the case of cyclodehydrating high molecular weight polyamic acids, TFAA gave erratic results and usually required repetitive treatment to effect complete isoimidization. Furthermore, polymer chain scission probably took place via acid hydrolysis. As a result, the polyisoimide products had low inherent viscosities.

Cyclodehydration of high-molecular-weight polyamic acids with N,N'-dicyclohexylcarbodiimide (DCC) yielded polyisoimides of high inherent viscosities. The completeness of conversion was measurable by the amount of N,N'-dicyclohexylurea (DCU) generated during

TABLE 5. REPRESENTATIVE POLYMERIZATION EXPERIMENTS

Experiment	Monomer Constituents	Polyamic Acid**		Polyisoimide**			Comment
		Solvent	Inherent Viscosity Measured at 30°C (η)	Solvent	Dehydrative Agent	Inherent Viscosity Measured at 30°C (η)	
1	PMDA-ODA	DMAC	0.53	—	—	—	
2	BTDA-ODA	DMAC	0.47	DMAC	TFAA	0.38	FTIR showed no amic acid
3	BTDA-ODA	DMAC	0.60	DMAC	TFAA	—	No conversion
4	6FDA-ODA	THF	0.22	—	—	—	Did not proceed with isoimidization due to low η of amic acid
5	6FDA-ODA	DMAC	0.26	—	—	—	Same
6	6FDA-6FNH$_2$	THF	0.22	—	—	—	Same
7	6FDA-ODA	DMAC	0.57	DMAC	TFAA	0.45	FTIR showed no amic acid
8	6FDA-ODA	DMAC	0.53	DMAC	TFAA	0.42	Recycling was necessary to complete conversion
9	6FDA-ODA	DMAC	0.97	THF	TFAA	0.30	Recycling three times
10	6FDA-ODA	DMAC	1.07	m-cresol	Δ	0.80	Product is polyimide
11	6FDA-ODA	DMAC	1.07	DMAC	Ac_2O, C_5H_5N	0.67	Polyimide
12	6FDA-ODA	DMAC	1.00	THF	(50% xs) DCC	0.50	FTIR showed no amic acid

(Continued next page)

TABLE 5. REPRESENTATIVE POLYMERIZATION EXPERIMENTS (Continued)

Experiment	Monomer Constituents	Polyamic Acid**		Polyisoimide**			Comment
		Solvent	Inherent Viscosity Measured at 30°C (η)	Solvent	Dehydrative Agent	Inherent Viscosity Measured at 30°C (η)	
13	6FDA-ODA	THF	not isolated	THF	(no xs) DCC	0.58 0.69(DMAC)	FTIR showed no amic acid
14	6FDA-ODA	NIP	0.33	THF	(small xs) DCC	0.25	Same
15	6FDA-ODA	THF	1.35	THF	(Small xs) DCC)	0.97	Same
16	6FDA-ODA	THF	not isolated	THF	(10% xs) DCC	0.91 0.96	After careful purification the η value was improved to 1.11
17	PMDA-BAPB	THF	—	THF	(small xs) DCC	0.38	FTIR showed no amic acid
18	BFTDA-ODA	THF	0.16	—	—	—	Isoimidization was not carried out in view of low η values for amic acid samples
19	BFTDA-6FNH$_2$	THF	0.16	—	—	—	Same
20	BFTDA-6FNH$_2$	NIP	0.17	—	—	—	Same
21	BFTDA-ODA	THF	0.29	—	—	—	Same
22	BFTDA-ODA	THF	not isolated	THF	(small xs) DCC	0.48	BFTDA used was recrystallized 3 times. FTIR indicated only isoimide was present in final product
23	BFTDA-MDAB	THF	not isolated	THF	(small xs) DCC	0.28	
24	BFTDA-ODA	THF	not isolated	THF	(small xs) DCC	0.27	

(Continued next page)

TABLE 5. REPRESENTATIVE POLYMERIZATION EXPERIMENTS (Concluded)

Experiment	Monomer Constituents	Polyamic Acid**		Polyisoimide**			Comment
		Solvent	Inherent Viscosity Measured at 30°C (η)	Solvent	Dehydrative Agent	Inherent Viscosity Measured at 30°C (η)	
25	BFDA-MDAB	THF	not isolated	THF	(small xs) DCC	0.30	
26	BFDA-ODA	THF	not isolated	THF	(small xs) DCC	—	BFDA was recrystalized 2 times

PMDA = Pyromellitic Dianhydride
ODA = 4,4′-Diaminodiphenyl Ether (4,4′-Oxydianiline)
BTDA = Benzophenonetetracarboxylic Dianhydride
6FDA = 2,2-Bix(3,4-dicarboxyphenyl)hexafluoropropane Dianhydride
$6FNH_2$ = 2,2-Bis(3-aminophenyl)hexafluoropropane
BAPB = 1,3-Bis(3-aminophenoxy)benzene
MDAB = 1,3-Diaminobenzene (m-phenylenediamine)
BFDA = 2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane Dianhydride
BFTDA = 2,2-Bis[4-(3,4-dicarboxythiophenoxy)phenyl]hexafluoropropane Dianhydride
DMAC = N,N-Dimethylacetamide
THF = Tetrahydrofuran
NIP = N-Isopropylpyrrolidinone
TFAA = Trifluoroacetic Anhydride
DCC = N,N′-Dicyclohexylcarbodiimide
Ac_2O = Acetic Anhydride

*Inherent viscosity measurement was carried out in the same solvent used in polymerization or dehydration reaction, unless otherwise indicated.

**The isolated polymer samples were dried under vacuum at various temperatures. It was determined that drying at 90–100°C at 0.1 torr gave the best results.

the reaction. A reliable quantitative method has been developed based on Fourier-Transform infrared (FTIR) spectroscopy to ascertain the presence of unreacted amic acid units (Reference 181). It was apparent that a higher amount of unreacted amic acid units was present in isoimide polymer samples of higher molecular weight. Extending the reaction time for the cyclodehydration step or carrying out the reaction at a higher dilution afforded only slight improvements.

Rate of Precipitation of Polymer. After the isoimidization step, the precipitated N,N'-dicyclohexylurea was removed by filtration and the polymer solution was concentrated to 50% of the initial volume and added to hexane which was stirred vigorously. The rate of addition of the THF polymer solution to hexane determined the amount of occluded impurities. The best results were obtained when the polymer solution was added dropwise but rapidly from an addition funnel. The precipitated polyisoimide polymer was then further purified by redissolving in anhydrous THF, filtering and reprecipitating in hexane.

Effect of Aluminum Oxide Treatment. Both neutral and basic aluminum oxide were tested as potential agents for the removal of residual amic acid contents in polyisoimide samples. A typical experiment was carried out with a 5% solution of 1 gram of poly(6FDA-ODA)isoimide in tetrahydrofuran (THF) and 1 gram of aluminum oxide. After stirring for 1 hour at 25°C, the polymer solution was filtered to remove aluminum oxide and mixed with hexane to reprecipitate the polymer. Normalized against a skeletal absorption at 1480 cm^{-1}, the relative peak heights due to amic acid (1540 cm^{-1}), isoimide (936 cm^{-1}) amd imide (1375 cm^{-1}), respectively, in the FTIR spectra, taken of the polymer before and after the alumina oxide treatment, were compared. The details of this analytical technique have been described (Reference 181). The results indicated that neutral aluminum oxide eliminated $>$ 95% of the residual amic acid units. Basic alumina oxide, by comparison, was less effective. The inherent viscosities of the polymer samples after the aluminum oxide treatment were lowered by approximately 13% (Table 6). It was not certain if this was a consequence of partial depolymerization or selective adsorption of the longer polymer molecules to the alumina surface.

TABLE 6. EFFECT OF ALUMINUM OXIDE TREATMENT

	Inherent Viscosity, η (in THF, at 20°C)		
	Untreated	Basic Al_2O_3	Neutral Al_2O_3
6FDA-ODA isoimide polymer from experiment 15	0.97	0.86	0.85

Volatile Content. Preliminary TGA-MS results obtained for high molecular weight polyisoimides indicated that the presence of residual organic solvents and moisture was inevitable using conventional drying procedures. During rheometric measurements, the entrapped volatiles present a serious outgassing problem in obscuring the direct observation of the cure process. In view of the successful application of supercritical fluids (notably carbon dioxide) as an extraction technique (References 187-189) in separation and purification, we carried out a preliminary evaluation of supercritical carbon dioxide as a means to remove trace amounts of occluded solvent and other volatiles from polyisoimides. As a solvent, carbon dioxide has several advantages, including low toxicity, flammability and cost. Polyisoimide samples were subjected to supercritical carbon dioxide processing. The standard procedure was to recycle 4 times from 2,000—8,000 psi (13.8—55.2 MPa, 1 psi = 6.894×10^{-3} MPa) with 30-minute holdings at 8,000 psi. Results from outgassing experiments (Table 7) carried out on polymer samples before and after the carbon dioxide treatment showed that this cleaning procedure was effective in the reduction of volatiles. Due to the nonpolar nature of carbon dioxide, the removal of polar impurities, e.g., residual trace of N,N'-dicyclohexylurea, was less effective. An internal study at Hughes is conducted to evaluate the applicability of supercritical fluid admixtures (such as carbon dioxide/5% methanol) to the removal of polar impurities from polymers.

TABLE 7. RESULTS OF OUTGASSING* EXPERIMENTS WITH POLYISOIMIDES

SAMPLE	MONOMER CONSTITUENT	INHERENT VISCOSITY OF POLYMER	% VOLATILES IN SAMPLE BEFORE CO_2	% VOLATILES IN SAMPLE AFTER CO_2	EFFICIENCY IN VOLATILE REMOVAL
K1543-105	(PMDA-BAPB)	0.41	7.73	1.93	0.75
V1-129-B	(BFTDA-ODA)	0.29	2.63	1.45	0.45
V1-137-B2	(6FDA-ODA)	1.10			
V1-127-A	(6FDA-ODA) amic acid	1.35			
V1-127-B	(6FDA-ODA)	0.97			
K1543-113	BTDA-BAPB oligomer		4.51(6.0)**	1.64(1.0)**	0.64(0.83)
K1543-134	6FDA-ODA oligomer		6.50	0.76	0.88
K1543-132	6FDA-ODA oligomer		8.31	0.56	0.93

*The outgassing experiment was conducted according to ASTM-E-595-77 at 125°C for 24 hours with the condenser plate maintained at 25°C and with a vacuum of 10^{-5} torr.

**Weight loss determined at 210°C in conjunction with TGA-MS analysis.

A detailed thermogravimetric-mass spectrometric (TGA-MS) analysis was carried out on one polyisoimide sample. The major volatile reduction effected by the supercritical carbon dioxide process was in relatively non-polar solvents. The other detected impurities, indole and cyclohexenimine, were reduced by 50%. N,N'-dicyclohexylurea was not removed by this method (Table 8).

TABLE 8. EVALUATION OF SUPERCRITICAL CO_2 PROCESS BY TGA-MS

Product Detected By MS	Mass ion at m/e	INTENSITY		Reduction Factor
		Before CO_2 Treatment	After CO_2 Treatment	
Solvents	43	96800	1690	0.02
(THF, methylpentane, etc.)	41	132600	2650	0.02
	57	90600	750	0.01
Indole	117	2020	1110	0.5
Cyclohexenimine	97	1600	970	0.5
Dicyclohexylurea	143	20	40	—*
CO	28	165000	171000	—
CO_2	44	62000	92000	—
H_2O	18	62000	79000	—

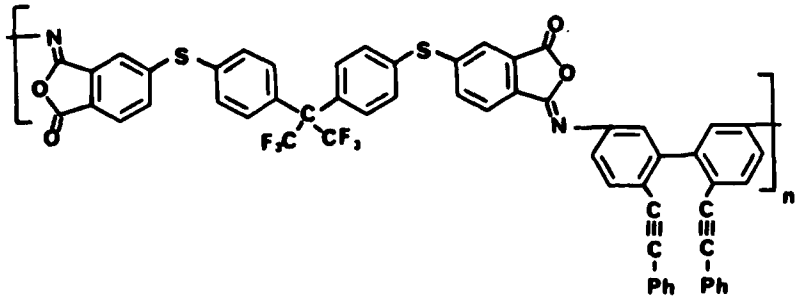
*Within the limits of uncertainty, there was no reduction.

All of the polyisoimide samples of $\eta > 0.5$ did not melt below 260°C. Under the processing conditions of 500 psi (3.45 MPa) and 230°C, they coalesced into semi-transparent discs. Preliminary cure studies showed that poly(PMDA-BAPB) isoimide exhibited a small differential between the isoimide Tg and the imide Tg (after cure). The imide Tg was below 275°C. By comparison, poly(6FDA-ODA) isoimide exhibited a Tg at 250°C and underwent cure to yield the corresponding imide that showed a Tg of 336°C. The results on the physiochemical evaluation of polyisoimides will be the subject of another AFWAL report.

Polyisoimide With IMC Capability

It was apparent from preliminary cure studies that high molecular weight polyisoimides do not melt to a fluid state at temperatures below 260°C. The best Tg advancement provided by the thermal conversion of isoimide to imide was approximately 75°C. In theory, an isoimide polymer derived from 2,2-bis[4-(3,4-dicarboxythiophenoxy)phenyl]hexafluoropropane dianhydride (BFTDA) and 5,5'-diamino-2,2'-bis(phenylethynyl)biphenyl (9) (vide supra) could have the added benefit of a second cure (rigidization) mechanism by virtue of the now well-known IMC reaction.

Both monomers were synthesized for the eventual polymerization studies. The preliminary set of experiments did not yield polymers of appreciable inherent viscosities. This set back was attributed probably to the inherent difficulties in the synthetic methods in yielding high purity materials.



SECTION III

EXPERIMENTAL

General Data

Infrared spectra were recorded on either a Beckman Acculab 6 spectrometer or a Nicolet MX-1 Fourier transform spectrometer. Liquid chromatography was performed using a Beckman Model 345 ternary liquid chromatograph. Proton magnetic resonance spectra were recorded on either a Varian EM-360L spectrometer or a Varian FT 80-A Fourier transform spectrometer. Carbon magnetic resonance and 250-MHz proton magnetic resonance spectra were obtained using a Bruker WM-250 Fourier transform spectrometer. Mass spectral analyses were performed using a Finnigan OWA/1000 GC-MS spectrometer equipped with a 30-meter SE-54 fused silica capillary, I.D. 0.25 mm. Microanalytical services were provided by Galbraith Laboratories, Inc., Knoxville, Tennessee and MicAnal Organic Microanalysis, Tucson, Arizona. Thermogravimetric-Mass Spectrometric (TGA-MS) analyses were performed by Systems Research Laboratories, Inc., Dayton, Ohio.

Differential scanning calorimetric (DSC) analyses were performed using either a DuPont 901 cell with a DuPont 990 thermal analyzer, or a DuPont 910 DSC cell in conjunction with a DuPont 1090 thermal analyzer. Thermomechanical analyses (TMA) were performed on either the DuPont 941 TMA module with the DuPont 990 thermal analyzer, or the DuPont 943 TMA module with the DuPont 1090 thermal analyzer. Thermogravimetric analyses (TGA) were performed on either the DuPont 950 TGA module with the DuPont 990 thermal analyzer, or the DuPont 951 TGA module with the DuPont 1090 controller.

Gel permeation chromatography (GPC) was performed using a Model 112 solvent delivery system, appropriate microspherogel columns, and a model 160 ultraviolet absorbance detector, all supplied by Beckman Instruments. GPC calculations were obtained on a Hewlett-Packard 85 microcomputer connected to the absorbance detector through a 760 series A/D converter supplied by Nelson Analytical; the software 390T Rev. 2.0, on cassette, was also supplied by Nelson Analytical.

1,2-Diacetamidobenzene

A slurry of 50.0 g (0.46 mole) of ortho-phenylenediamine in 330 ml of water was treated with 86 ml (79 g, 0.92 mole) of acetic anhydride. After the exotherm was spent, the mixture

appeared beige yellow. The crystals were filtered, washed with cold water and dried at 100°C/0.1 torr for 16 hr. The yield was 68.3 g (0.36 mole, 78.3%); mp 188–188.5°C [lit. value: 189–190°C (Reference 84), 185–186°C (Reference 85)]; IR (KBr) showed the presence of carbonyl and NH absorptions; MS (70 eV) m/e 192 (molecular ion), 108 (base peak); ^{1}H NMR ($CDCl_3$) δ 2.05 (s, 6H, $NHCOCH_3$), 7.10 (m, 4H, aromatic) and 8.30 ppm (bs, 2H, NH).

4-Bromo-1,2-diacetamidobenzene

A solution of 53.9 g (0.280 mole) of 1,2-diacetamidobenzene in 300 ml of glacial acetic acid was cooled at 0°C and treated by dropwise addition with a 40-ml volume of acetic acid containing 44.8 g (0.280 mole) of bromine. The precipitate was difficult to stir and enough methanol was added to maintain stirring. After complete addition, the mixture was allowed to rise to ambient temperature, diluted with 2.5 liters of water and filtered. The white voluminous precipitate was thoroughly dried at 80°C/0.1 torr for 16 hr. Recrystallization from ethanol and subsequent drying at 80°C/0.1 torr for 4 hr gave 34.6 g (0.128 mole, 45.6%) of white, fluffy crystals: mp 214–218°C; IR (KBr) showed the expected absorptions for C=O and NH; MS (70 eV) revealed a slight contamination with the dibromo derivative; ^{1}H NMR (DMSO-d_6) δ 1.95 (s, 6H, $COCH_3$), 7.00–7.75 (m, 3H, aromatic) and 9.40 ppm (bs, NH).

Elemental analysis showed a high bromine value.

Anal. for $C_{10}H_{11}BrN_2O_2$ (271.13):

Calculated: C, 44.42; H, 4.07; N, 10.36; Br, 29.29.
Found: C, 43.93; H, 4.00; N, 10.04; Br, 32.58.

Formation of 4-Acetamido-6-bromo-2-methylbenzoxazole and 2-Acetamido-5-bromo-1,4-benzoquinone. Reaction of 4-Bromo-1,2-diacetamidobenzene with Thallium[III] Trifluoroacetate

Under argon, 40.6 g (7.50 mmoles) of thallium[III] trifluoroacetate (TTFA) was weighed out and dissolved in 35 ml of trifluoroacetic acid. The solution was then quickly added to 4.05 g (15.0 mmoles) of 4-bromo-1,2-diacetamidobenzene under argon. The red-brown reaction mixture was stirred and heated at reflux (73°C) for 2 hrs in the dark. Half of the trifluoroacetic acid solvent was removed by distillation and the concentrate was poured into 200 ml of water. The aqueous mixture was then extracted four times with 50-ml portions of chloroform. The chloroform extracts were combined, washed with 200 ml of saturated aqueous sodium bicarbonate and then with 200 ml of water, and dried over anhydrous magnesium sulfate. After solvent removal, the solid residue was extracted with ether to separate the soluble

products from the unreacted starting material. The impure product mixture was then purified by silica gel column chromatography to give first 110 mg (0.453 mmole, 3.02%) of pure 2-acetamido-5-bromo-1,4-benzoquinone (17) in the chloroform eluate and then 1.00 g (37.2 mmoles, 24.8%) of pure 4-acetamido-6-bromo-2-methylbenzoxazole (16) in the 1 : 1 chloroform-ether eluate. No reaction occurred when the reactant mixture was stirred for 2 hrs at 20 to 25°C. Extension of the reflux period to 24 hrs did not increase the yield of products. When double the theoretical amount of TTFA was used, the yields were not increased, but there was a larger amount of highly colored impurities. Washing the chloroform extracts with saturated aqueous sodium bicarbonate was absolutely necessary, for no pure product was isolated when the washing was omitted.

Compound 16 was isolated as a white crystalline solid and gave a positive Beilstein test; mp 160.5–162°C; IR (KBr) 3300, 1680, 1630, 1530, 1400 and 1270 cm $^{-1}$; MS (70 eV) m/e 268, 270 (molecular ions); ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H, $COCH_3$), 2.67 (s, 3H, $CH_3C{=}N-$), 7.38 (d, 1H, J = 2 Hz, H_5), 8.15 (broad s, 1H, NH), and 8.48 ppm (d, 1H, J = 2 Hz, H_7).

Anal. for $C_{10}H_9BrN_2O_2$ (269.11):

Calculated: C, 44.63; H, 3.37; N, 10.41.
Found: C, 44.50; H, 3.65; N, 10.21.

Compound 17 was crystallized from dichloromethane-hexane as lustrous golden platelets which gave a positive Beilstein test; mp 186°C; IR (KBr) 3300, 1700, 1670, 1640, 1590, 1510, and 1325 cm $^{-1}$; MS (70 eV) m/e 243, 245 (molecular ions); ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 3H, $COCH_3$), 7.33 (s, 1H, H_6), 7.83 (s, 1H, H_3), and 8.00 ppm (broad s, 1H, NH).

Anal. for $C_8H_6BrNO_3$ (244.05):

Calculated: C, 39.37; H, 2.48; N, 5.74; Br, 32.74.
Found: C, 39.35; H, 2.50; N, 5.71; Br, 33.10.

Note: A recommended treatment of toxic thallium waste is as follows:

The glassware is first rinsed thoroughly with acetone and then with 1N aqueous hydrochloric acid. The combined washings are treated with concentrated ammonium hydroxide and then with an aqueous solution of sodium sulfide. The wastes are transferred to a waste container (labelled for toxic wastes) for removal from premises.

1,2-Bis(4-toluenesulfonamido)-4-bromobenzene

In a 2-liter flask fitted with a reflux condenser were placed 108.1 g (1.00 mole) of o-phenylenediamine (MC & B), 400.4 g (2.10 moles) of 4-toluenesulfonyl chloride (Aldrich)

and 500 ml of anhydrous pyridine. The mixture was heated at reflux for 2 hr, allowed to cool and then poured into water with vigorous stirring. The solid obtained was filtered, washed well with water and dried in air, yielding a total of 452 g of a greyish solid. Recrystallization of one portion from glacial acetic acid afforded 184.9 g of purified product with a mp of 205.5–206.5°C. The remainder of the crude product was recrystallized from a large volume of ethanol, yielding 141.7 g (mp 204–205.5°C). The combined yield of 1,2-bis(4-toluenesulfonamido)benzene was 326.6 g (0.784 mole, 78.4%).

F. Reverdin and P. Crepieux, Chem. Ber., 35, 314 (1902); Beilstein, XIII, 25 gave the mp as 201–202°C.

Into a 500-ml three-neck flask fitted with an addition funnel, a mechanical stirrer, and a condenser were placed 83.2 g (200 mmoles) of 1,2-bis(4-toluenesulfonamido)benzene, 1 g of anhydrous ferric chloride, and 1200 ml glacial acetic acid. The mixture was warmed to 90°C to dissolve all the solid. The temperature of the stirred solution was maintained at 75–80°C and the mixture was treated by dropwise addition with 36.8 g (230 mmoles) of bromine in 50 ml glacial acetic acid over 15 minutes. The solution was stirred for 45 minutes longer without heating, then cooled to ambient temperature, diluted with 2.5 liters of water and filtered to give a reddish solid which was recrystallized from glacial acetic acid: yield, 53.4 g (107.8 mmoles, 53.9%); mp 196–199°C; IR (KBr) showed intense absorptions of NH groups; MS (70 eV) m/e 495 (molecular ion); ^{1}H NMR (DMSO-d_6) δ 2.40 (s, 6H, CH_3), 7.04 (d, 1H, aromatic H_6), 7.18 (d×d, 1H, aromatic H_5), 7.26 (bs, 1H, aromatic H_3), 7.26, 7.41, 7.59, 7.72 (AB q, J = 9 Hz, aromatic H's on tolyl), and 9.50 ppm (broad absorption, 2H, NH).

Anal. for $C_{20}H_{19}BrN_2O_4S_2$ (495.42):

Calculated: C, 48.48; H, 3.87; N, 5.66; S, 12.94; Br, 16.13.
Found: C, 49.41; H, 3.98, N, 5.74; S, 13.28; Br, 16.12.

Reaction of 1,2-Bis(4-toluenesulfonamido)-4-bromobenzene with Thallium[III] Trifluoroacetate

Into a 250-ml three-neck flask equipped with a reflux condenser and magnetic stirrer were placed 10.0 g (20.2 mmoles) of 1,2-bis(4-toluenesulfonamido)-4-bromobenzene and 22 ml of trifluoroacetic acid (TFA). In a glove bag under argon atmosphere, 5.50 g (10.1 mmoles) of thallium[III] trifluoroacetate (TTFA) was measured out and dissolved in 35 ml of TFA. The TTFA/TFA reagent was then transferred to an addition funnel which was positioned on the three-neck flask. The dropwise addition of the thallium reagent to the substrate solution caused the appearance of a dark red color. After the addition, the reaction flask was covered with aluminum foil and was heated at reflux for 2 hrs. Most of the TFA solvent was removed

by distillation and the concentrate was poured into 250 ml of water and extracted three times with 75-ml portions of chloroform. The combined chloroform extracts were washed with 200 ml each of saturated sodium bicarbonate and water. After drying over anhydrous magnesium sulfate, the chloroform solution was evaporated to leave a solid which was purified by silica gel column chromatography with 1 : 9 methanol-dichloromethane as eluant. Several crops of crystals were obtained that appeared to be the same material by thin-layer chromatography. One crop was recrystallized from hot aqueous acetic acid and dried at 100°C/0.1 torr, yielding beige brown crystals, mp 215–216°C. The bulk of the eluted material upon recrystallization from hot aqueous acetic acid gave a dark red crystalline solid, mp 205–212°C. A second recrystallization from the same solvent with charcoal treatment raised the mp to 208.5–212°C. The total yield of crystalline product was 7.42 g (15.1 mmole, 74.5%).

The crystalline product gave a positive Beilstein test and was identified as 7-bromo-2-(4-tolyl)-4-(4-tolylsulfonamido)-1,2,3-benzoxathiazole 2-oxide (18): IR (KBr) 3460, 1610, 1500, 1340, and 1175 cm $^{-1}$; MS (70 eV) m/e 492, 494 (molecular ions); ^{1}H NMR (DMSO-d_6) δ 2.36 (s, 6H, CH_3), 6.75–7.80 (m, 10H, aromatic) and 9.30 ppm (broad s, 1H, NH).

Anal. for $C_{20}H_{17}BrN_2O_4S_2$ (493.40):

Calculated: C, 48.69; H, 3.52; Br, 16.20; N, 5.68; S, 13.00.
Found: C, 48.37; H, 3.86; Br, 15.97; N, 5.57; S, 13.01.

Attempted Telluration of 1,2-Diacetamidobenzene

Into a 250-ml three-neck flask equipped with a thermometer and a reflux condenser were placed 10.0 g (52.0 mmoles) of 1,2-diacetamidobenzene and 20 ml of triglyme (bp 70°C/40 torr, freshly distilled from sodium). Inside a glove bag and under argon, 7.02 g (26.0 mmoles) of tellurium[IV] chloride was measured and transferred to the reaction flask with 20 ml of triglyme. The mixture was quickly heated to 160°C and maintained at the same temperature for 6 hr. The triglyme solvent was removed at 1 torr and the fine black solid residue gave an unintelligible NMR spectrum. IR (KBr) indicated that no carbonyl absorption was present. No further characterization was carried out.

4-Amino-3-nitrophenylmercuric Acetate and the Intermediate Oxy-Mercury Complex

Upon mixing a solution of 18.4 g (57.8 mmoles) of mercuric acetate in 75 ml of water with a solution of 9.40 g (68.1 mmoles) of o-nitroaniline in 100 ml of ethanol, an orange red precipitate formed instantaneously. A few drops of glacial acetic acid were added and the mixture was heated to a gentle reflux. After 30 min, a reddish brown color developed. The

mixture was then treated with 75 ml of glacial acetic acid. A dramatic change of color to bright yellow took place. After cooling to room temperature and filtering, the bright yellow solid appeared microcrystalline and was washed with cold ethanol and then with ether. The product was thoroughly dried at 80°C/0.1 torr for 16 hr: yield, 20.4 g (51.4 mmoles, 89.0%); mp >300°C (blackening occurred at 270–275°C); IR (KBr) 3480, 3360, 3340, 1635, 1580, 1500, 1260 cm $^{-1}$; ^{1}H NMR (DMSO-d_6) δ 2.00 (s, 3H, $COCH_3$), 7.20 (q, 2H, aromatic H_5H_6 AB quartet), 7.40 (broad absorption, 2H, NH_2) and 8.05 ppm (distorted s, 1H, aromatic H_2).

In the absence of glacial acetic acid, the mixing of a solution of 4.20 g (30.4 mmoles) of o-nitroaniline in 300 ml of ethanol and a solution of 9.60 g (30.2 mmoles) of mercuric acetate in 100 ml of water yielded an orange red powdery precipitate which was isolated by filtration and washed with ethanol and then with ether: yield, 6.60 g (13.9 mmoles, 91.4%); softened at 312°C, gradually turned black upon heating to 340°C; IR (KBr) 3360, 1620, 1615, 1560, 1500, 1360 cm $^{-1}$; ^{1}H NMR (DMSO-d_6) δ 6.47 (m, 1H, aromatic H_6), 7.27 (m, 2H, aromatic H_4 and H_5), 7.82 (d×d, 1H, aromatic H_3), and 8.10 ppm (broad s, 1H, NH).

Upon treatment with an aqueous solution of sodium sulfide, a sample of the orange red oxy-mercury complex immediately dissolved and quickly yielded the black precipitate of mercuric sulfide. This test showed inorganic mercury in the oxy complex.

3,3′-Dinitrobenzidine

A mixture of 4.00 g (10.1 mmoles) of 4-amino-3-nitrophenylmercuric acetate, 3.00 g (47.2 mmoles) of copper powder and 100 mg (0.56 mmoles) of palladium chloride in 125 ml of anhydrous pyridine was deaerated with argon, heated at reflux for 24 hr, filtered while hot through Celite and the solid residue was washed with 300 ml of warm benzene. The filtrate was cooled and extracted two times with 500-ml portions of 15% aqueous ammonium hydroxide, twice with 500-ml portions of 10% aqueous hydrochloric acid, twice with 500 ml of water and then twice with 15% aqueous ammonium hydroxide. The organic fraction was dried over anhydrous magnesium sulfate and concentrated to yield a red powdery solid. The magnesium sulfate residue was extracted twice with 500 ml of boiling toluene. The combined toluene extracts yielded another batch of red powder after solvent removal. The red powder gave a sharp mp at 280°C: yield, 950 mg (3.47 mmoles, 68.7%); IR (KBr) 3480, 3370, 1640, 1510, 1360, 1250 cm $^{-1}$; ^{1}H NMR (DMSO-d_6) δ 7.10 (d, 1H, aromatic H_5), 7.70 (d×d, 1H, aromatic H_6), 8.10 (d, 1H, aromatic H_2), and 7.45 ppm (bs, 2H, NH).

2,2′-Dibromobiphenyl

The procedure in Reference 90 was adopted. Into a flame-dried 500-ml three-neck flask equipped with an addition funnel and a low-temperature thermometer and purged with

argon were placed 25.0 g (0.106 mole) of 1,2-dibromobenzene and 250 ml of anhydrous tetrahydrofuran. While the reaction mixture was cooled to −78°C, 34.4 ml (55.0 mmoles) of a 1.6M solution of n-butyllithium in hexane was transferred from the stock bottle to the addition funnel using the double-tipped needle technique. At −78°C, dropwise addition of the lithium reagent to the substrate solution was commenced and was maintained at such a rate that the reaction temperature did not rise more than 5°C. The entire addition required one hour. The mixture was then warmed to +5°C and hydrolyzed with 60 ml of 1N aqueous hydrochloric acid. The phases were separated and the aqueous phase was extracted four times with 50-ml portions of ether. The combined organic extracts were dried over anhydrous magnesium sulfate and concentrated to a viscous oil which crystallized upon cooling. Recrystallization from absolute ethanol yielded 2 crops of white needles: yield, 13.4 g (42.9 mmoles, 80.9%); mp 79–80°C; MS (70 eV) m/e 314, 312, 310 (molecular ions), 231, 233 (loss of 1 Br), 152 (base peak, loss of 2 Br); ^{1}H NMR ($CDCl_3$) δ 7.00–7.80 ppm (complex m, aromatic).

2,2′-Dibromo-3,3′,5,5′-tetranitrobiphenyl

A 1-liter three-neck flask was charged with 77 ml of concentrated sulfuric acid and 130 ml of 90% (fuming) nitric acid. The solution was heated under a gentle reflux while a solution of 11.6 g (37.2 mmoles) of 2,2′-dibromobiphenyl in 84 ml of concentrated sulfuric acid was added dropwise. After the addition, the refluxing reaction mixture was treated by dropwise addition with another solution of 95 ml of fuming nitric acid in 112 ml of concentrated sulfuric acid. The final mixture was heated for an additional 4 hr, cooled, and poured into 1 liter of ice water. A flocculent pale yellow solid was isolated by filtration and dried at 100°C/0.1 torr for 8 hr. Recrystallization from acetone-methanol yielded pale yellow crystals: 17.7 g (36.0 mmoles, 96.8%); mp > 300°C; IR (KBr) 3100, 1545, 1350 cm^{-1}; MS (70 eV) m/e 494, 492, 490 (weak molecular ions), base peak at m/e 411; ^{1}H NMR (DMSO-d_6) δ 8.68 (d, 1H, J = 3 Hz, aromatic C_6) and 9.06 ppm (d, 1H, J = 3 Hz, aromatic C_4).

Anal. for $C_{12}H_4Br_2N_4O_8$ (492.01):

Calculated: C, 29.29; H, 0.82; N, 11.39; Br, 32.48.
Found: C, 29.41; H, 0.82; N, 11.41; Br, 32.46.

2,2′-Dibromo-5,5′-dinitrobiphenyl

The literature procedure (Reference 92) was adopted. To a stirred solution of 6.43 g (20.6 mmoles) of 2,2′-dibromobiphenyl in 25 ml of dichloromethane was added 100 ml of concentrated sulfuric acid. The mixture was cooled at 0–5°C and then treated by dropwise addition

with 30 ml of nitric acid (70% assay). The bath temperature was maintained at 0–5°C through the addition. The resulting turbid yellow mixture was stirred at 25°C for 2 hr, poured into 1 liter of water and extracted three times with 200-ml portions of dichloromethane. The combined organic extracts were dried over magnesium sulfate and concentrated to a yellow solid. Recrystallization from 1 : 3 acetone-ethanol yielded pale yellow crystals: 5.40 g (13.4 mmoles, 65.2%); mp 220–221°C; IR (KBr) 3110, 3090, 1601, 1530 (intense), 1450, 1360 (intense) cm $^{-1}$; ^{1}H NMR (DMSO-d_6) δ 7.14 (s, 1H, aromatic H_6) and 6.90–7.30 ppm (distorted AB quartet, 2H, aromatic H_3 and H_4).

The mother liquor from the recrystallization process yielded a second powdery solid which by ^{1}H NMR was 2,2′-dibromo-3,5′-dinitrobiphenyl, mp 117–119°C.

2,2′-Diiodobiphenyl

To a solution of 40.0 g (0.128 mole) of 2,2′-dibromobiphenyl in 200 ml of anhydrous ether at 0°C was added dropwise 176 ml of a 1.6M solution of n-butyllithium in hexane. The mixture was stirred at 25°C for 2 hr, cooled to 0°C and treated with 72 g of iodine in 300 ml of anhydrous ether. At the end, the mixture acquired a brown tint indicating a slight excess of iodine. The solution was allowed to stand 16 hr at 25°C before washing with 300 ml each of water, 20% aqueous sodium bisulfite, saturated sodium bicarbonate and then water. The organic phase was finally separated, dried over anhydrous magnesium sulfate and concentrated to a white solid mass. Recrystallization from methanol with charcoal treatment gave 41.5 g (0.102 mmoles, 79.9%) of white rhombic crystals, mp 107–108°C (a second recrystallization raised the mp to 109–110°C); ^{1}H NMR ($CDCl_3$) δ 6.96–7.56 (symmetrical multiplet, 3H, aromatic H_4, H_5, H_6) and 7.05 ppm (distorted doublet, 1H, J's = 8.0 Hz, 1.0 Hz, aromatic H_3).

Attempted Synthesis of 2,2′-Diiodo-5,5′-dinitrobiphenyl by Nitration with Nitric Acid

A solution of 6.60 g (13.3 mmoles) of 2,2′-diiodo-5,5′-dinitrobiphenyl in 25 ml of dichloromethane was mixed with 50 ml of concentrated sulfuric acid. Stirred at 0°C, the mixture was treated by dropwise addition with 20 ml of 70% nitric acid. The mixture turned dark brown. After 2 hr at 25°C, it was diluted with 1 liter of water and extracted three times with 100-ml portions of dichloromethane. The combined extracts were dried and concentrated. The powdery solid (mp 280°–283°C) obtained was not soluble in methanol and only very sparingly soluble in dichloromethane.

The experiment was repeated at −15°C. The product isolated at the end of the work-up process was again not soluble in methanol or dichloromethane. The IR spectrum showed strong hydroxy and nitro absorptions.

2,2′-Diiodo-5,5′-dinitrobiphenyl

a. Mixture of Nitronium Triflate and Hydronium Triflate as Nitrating Agent

Into a flame-dried, argon-purged three-neck flask were placed 50 ml of anhydrous dichloromethane, 4.0 ml (6.5 g) of trifluoromethanesulfonic acid and then 1.0 ml (1.4 g) of anhydrous nitric acid (freshly distilled from sulfuric acid). The slurry was stirred at 25°C for 30 min, cooled to 0°C, and then treated with 3.9 g (9.6 mmoles) of 2,2′-diiodobiphenyl in 20 ml of anhydrous dichloromethane. The mixture was allowed to warm to 25°C over 2.5 hrs, and was poured into 200 ml of water. The organic phase was separated, washed with 2 × 100 ml of saturated sodium bicarbonate solution and then with water, dried over anhydrous magnesium sulfate and concentrated to give 4.2 g (89%) of crude dinitro derivative. Recrystallization from 10% acetone in ethanol yielded 2.85 g (5.75 mmoles, 60.0%) of pale yellow crystalline product: mp 236–238°C; IR (KBr) 1596, 1555, 1514 (intense), 1346 (intense), 1020, 1010, 854, 832, 740 cm $^{-1}$; ^{1}H NMR (DMSO-d_6) δ 8.01, 8.15 (d×d, 1H, J's = 8 Hz, 3 Hz, aromatic H_3) 8.30, 8.44 (d×t, 1H, J's = 9 Hz, 3 Hz, 0.5 Hz, aromatic H_4) and 8.15 ppm (s, 1H, aromatic H_6). The splitting pattern is an ABC system.

Anal. for $C_{12}H_6I_2N_2O_2$ (496.00):

Calculated: C, 29.06; H, 1.22; N, 5.65; I, 51.17.
Found: C, 29.08; H, 1.32; N, 5.49; I, 51.29.

The mother liquor obtained from recrystallization contained a mixture of the 5,5′-dinitro and the 3,5′-dinitro isomers as evident from NMR and HPLC analyses.

b. Homogeneous Nitronium Triflate Reagent

Into a flame-dried, argon-purged three-neck flask were placed 40 ml of anhydrous dichloromethane, 3.9 ml (7.1 g, 25 mmoles) of trifluoromethanesulfonic anhydride and then 1.1 ml (1.7 g) of anhydrous nitric acid. The mixture remained homogeneous. After 10 min at 25°C, the solution was cooled to 0°C and treated by dropwise addition with a deaerated solution of 50 g (12 mmoles) of 2,2′-diiodobiphenyl in 30 ml of anhydrous dichloromethane. The reaction was allowed to proceed for 14 hr at 25°C. The mixture was then poured into 500 ml of water and the organic phase was separated, washed with 100 ml of saturated sodium bicarbonate solution and 100 ml of water. After drying over anhydrous magnesium sulfate and solvent removal, a pale yellow solid residue was obtained. Recrystallization from acetone-ethanol yielded pale yellow crystals: 3.8 g (7.7 mmoles, 64%); mp 236–238°C, 239–241°C. ^{1}H NMR spectrometry ascertained the 5,5′-dinitro substitution pattern. High performance liquid chromatography showed that the compound was 97% isomerically pure.

2,2′-Bis(phenylethynyl)-5,5′-dinitrobiphenyl. Phenylethynylation of 2,2′-Diiodo-5,5′-dinitrobiphenyl with Copper[I] Phenylacetylide

A mixture of 1.986 g (4.004 mmoles) of 2,2′-diiodo-5,5′-dinitrobiphenyl and 1.400 g (8.509 mmoles) of copper[I] phenylacetylide in 50 ml of deaerated anhydrous pyridine was heated from 25°C to 110°C over 1 hr and kept at a gentle reflux for 16 hr. The mixture was diluted by pouring it into 500 ml of 10% aqueous hydrochloric acid and extracted three times with 100-ml portions of dichloromethane-ether. The combined organic extracts were dried over anhydrous magnesium sulfate and concentrated to a solid. Recrystallization from toluene gave light weight, bright yellow micro needles, 1.108 g (2.50 mmoles, 62.3%): mp 216–216.5°C; IR (KBr) 2200, 1600, 1572, 1494, very strong and broad NO_2 absorptions at 1515, 1340, 1350 cm^{-1}; MS (70 eV) m/e 444 (molecular ion); ^1H NMR ($CDCl_3$) δ 7.30 (distorted s, 5H, C≡C-Ph), 7.86 (d, 1H, J = 9 Hz, aromatic H_3), 8.35 (d×d, 1H, J's = 9 Hz, 2Hz, aromatic H_4) and 8.55 ppm (d, 1H, J = 2 Hz, aromatic H_6).

Phenylethynylation of 2,2′-Dibromo-5,5′-dinitrobiphenyl with Copper[I] Phenylacetylide

A deaerated mixture of 2.20 g (5.47 mmoles) of 2,2′-dibromo-5,5′-dinitrobiphenyl and 1.90 g (11.5 mmoles) of copper[I] phenylacetylide in 50 ml of anhydrous pyridine was heated from 25°C to 110°C for over 30 minutes and kept at 110°C for 24 hours under argon. The black mixture was diluted with an equal volume of dichloromethane and concentrated to a viscous syrup. Silica gel column chromatography yielded white crystalline 1,4-diphenylbutadiyne (mp 85–86°C) in the hexane eluate and a yellow solid in the 1:2 dichloromethane-hexane eluate. The yellow solid was recrystallized from 1:1 hexane-benzene to give 500 mg (1.13 mmoles, 20.6 percent) of bright yellow needle-like crystals of 2,2′-bis(phenylethynyl)-5,5′-dinitrobiphenyl: mp 216–216.5°C. The IR and ^1H NMR spectra were identical to those of an authentic sample.

Palladium-catalyzed Phenylethynylation of 2,2′-Dibromo-5,5′-dinitrobiphenyl

At 50°C, a partial solution of 5.40 g (13.4 mmoles) of 2,2′-dibromo-5,5′-dinitrobiphenyl and 3.00 g (29.4 mmoles) of phenylacetylene in 140 ml of deaerated 3:1 toluene-triethylamine was treated by sequential addition of 25 mg (0.036 mmole) of dichlorobis(triphenylphosphine) palladium[II], 300 mg (1.15 mmoles) of triphenylphosphine and 25 mg (0.132 mmole) of copper[I] iodide. The mixture was quickly heated to 100°C over 10 minutes. At this point, a

clear yellow solution was obtained. After 30 minutes, the solution gradually changed to a red-orange color and a precipitate began to accumulate. After 2 hours, the supernatant liquid turned dark reddish brown. Without cooling, the mixture was filtered. The brown solid mass was washed with boiling toluene until the solid changed into a fluffy white consistency. This white solid was soluble in cold water and had an IR spectrum identical tothat of triethylamine hydrobromide: yield, 4.40 g (92% of theory). The orange brown filtrate yielded orange yellow crystalline material, which was recrystallized from toluene to give golden yellow needles. The product was obtained analytically pure by silica gel column chromatography, with 1:1 hexane-dichloromethane as eluant: yield, 3.40 g (7.66 mmoles, 57.1%); mp $>$ 310°C; IR (KBr) 2180 (medium), very strong absorptions at 1515 and 1340 cm^{-1}; MS (70 eV) m/e at 444 (molecular ion); ^1H NMR (pyridine-d_5, 57°C) δ 6.79 (d, 1H, J = 8.7 Hz, fluorenyl H_8), 7.20-7.78 (3 m's, 10H, H's on pendent phenyls), 7.90 (d $\times$ d, 1H, J's = 8.7, 2.1 Hz, fluorenyl H_7), 8.48 (d $\times$ d, 1H, J's = 8.6, 2.1 Hz, fluorenyl H_2), 8.89 (d, 1H, J = 2.1 Hz, fluorenyl H_5), 8.97 (d, 1H, J = 2.1 Hz, fluorenyl H_4), and 9.14 ppm (d, 1H, J = 8.6 Hz, fluorenyl H_1).

Anal. for $C_{28}H_{16}N_2O_4$ (444.45):

Calculated: C, 75.67; H, 3.63; N, 6.30.
Found: C, 75.59; H, 3.69; N, 6.24.

Another experiment, using the same quantities of reactant, 17.63 mg of palladium[II] acetate and 65.52 mg of tris(o-tolyl)phosphine, led to the isolation of 3.20 g of the same orange yellow crystalline product, mp $>$ 315°C.

A further experiment using 2,2'-diiodo-5,5'-dinitrobiphenyl as starting material gave a 68% yield of the same yellow crystalline product (mp $>$ 315°C) as above, identified by IR, MS and NMR analyses.

Palladium-catalyzed Phenylethynylation of 2,2'-Diiodobiphenyl

A deaerated solution of 4.060 g (10.00 mmoles) of 2,2'-diiodobiphenyl and 2.261 g (22.20 mmoles) of phenylacetylene in 120 ml of anhydrous triethylamine was treated with a catalyst mixture comprising 46.2 mg of dichlorobis(triphenylphosphine)palladium[II], 87.3 mg of triphenylphosphine and 70.2 mg of copper[I] iodide. The cloudy yellow solution was stirred at 25°C for 10 minutes and gradually heated to 80°C over 30 minutes. At an internal temperature of 50°C, a flocculent white precipitate began to accumulate. The mixture was maintained at 80-85°C for 3 hours, then cooled, diluted with an equal volume of ether and filtered. The recovery of 4.123 g (90.0 % of theory) of white triethylamine hydriiodide indicated that the reaction was 90 percent completed.

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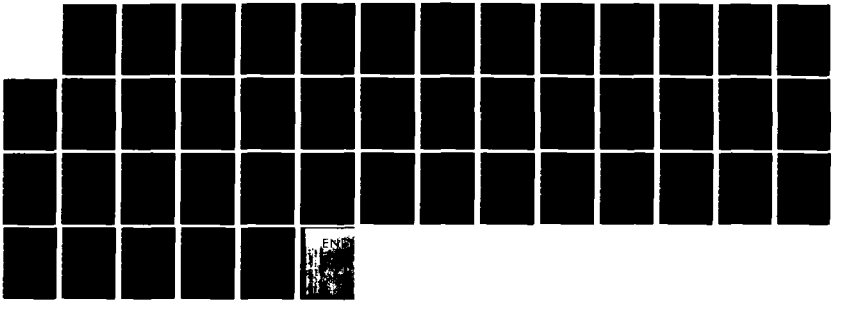

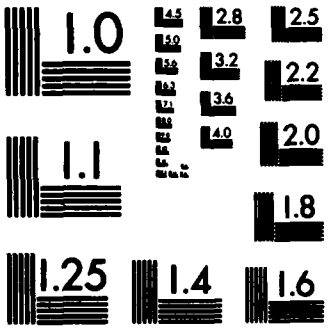

The yellow filtrate was concentrated to yield a solid residue which was recrystallized from hexane to give 2 crops of yellow crystals, totalling 2.757 g (7.70 mmoles, 77.9%) of 3-(fluoren-9-ylidene)-1,3-diphenylpropyne. Analytically pure, brilliant yellow crystals were obtained after chromatography through a silica gel column, eluting with 2 liters of 10% dichloromethane in hexane; the recovery after chromatography was 2.362 g (85.7%): mp 116–116.5°C; IR (KBr) 2200 (weak), 1505, 1460, 790, 765, 740, and 700 cm^{-1}; MS (70 eV) m/e 354 (molecular ion), 276 ($M^+ - C_6H_5$), 252 ($M^+ - C_6H_5C{\equiv}C$); 250-MHz ^1H NMR ($CDCl_3$) δ 6.47 (d x d, 1H, J's = 0.8, 8.0 Hz, fluorenyl H_8), 6.85 (d x d x d, 1H, J's = 1.0, 8.0, 8.0 Hz, fluorenyl H_7), 7.18 (d x d x d, 1H, J's = 0.8, 7.5, 8.0 Hz, fluorenyl H_6), 7.32–7.60 (overlapping m's, 12 H, fluorenyl H_2, H_3 and phenyl H's), 7.62 (d, 1H, J = 7.5 Hz, fluorenyl H_5), 7.68–7.70 (m, 1H, fluorenyl H_4), and 8.60–8.90 ppm (m, 1H, fluorenyl H_1); ^{13}C NMR ($CDCl_3$) δ 140.61, 140.56, 140.50, 140.15, 138.41, 137.78, 131.84, 129.22, 129.04, 128.70, 128.60, 127.57, 126.84, 125.71, 125.12, 123.47, 123.11, 119.63, 119.60, 102.46, and 92.24 ppm.

Anal. for $C_{28}H_{18}$ (354.45):

Calculated: C, 94.88; H, 5.12.
Found: C, 94.59; H, 5.36.

9-(Phenylethynyl)phenanthrene

9-Iodophenanthrene was synthesized from its bromo analog by the conventional lithiation-iodination method. To a deaerated solution of 25.7 g (100 mmoles) of 9-bromophenanthrene in 175 ml of anhydrous ether at 0°C was added dropwise 87.0 ml of a 1.5M n-butyllithium solution in hexane. The resulting mixture was kept at 0°C for 30 minutes and then warmed to 25°C. After 2 hours at 25°C, the mixture was cooled again to 0°C and treated with a solution of 33 g of iodine in 250 ml of anhydrous ether. The mixture was warmed to 25°C and kept at 25°C for 2 hours. The mixture was then washed with 300 ml each of water, 20% sodium bisulfite solution, and then water again. The ether phase was dried over anhydrous magnesium sulfate and concentrated to a solid, which was recrystallized from hexane to give fluffy crystals: 21.3 g (70.1 mmoles, 70.1%); mp 92°C (lit. mp 91–92°C); IR (KBr) weak absorptions at 1635, 1618, 1490, 1450, 1370, 1270, 1190, 900, 880, 845, and intense absorptions at 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45–7.80, 8.05–8.30, 8.40–8.65 (three m's, 8H, aromatic H_1 to H_8) and 7.39 ppm (s, 1H, aromatic H_9).

Anal. for $C_{14}H_9I$ (304.13):

Calculated: C, 55.29; H, 2.98; I, 41.73.
Found: C, 55.10; H, 2.99; I, 41.93.

A deaerated solution of 2.49 g (8.19 mmoles) of 9-iodophenanthrene in 100 ml of anhydrous triethylamine containing 22.6 mg of palladium[II] acetate, 62.1 mg of triphenylphosphine and 1.17 g (11.5 mmoles) of phenylacetylene was heated to 80–85°C for 18 hours. The mixture was cooled, mixed with 100 ml of ether, and filtered to remove 1.69 g (7.38 mmoles, 90.1%) of triethylamine hydroiodide.

The filtrate was washed with 100 ml each of 10% hydrochloric acid, water, saturated sodium bicarbonate solution, and water again. The organic phase was separated, dried over anhydrous magnesium sulfate and concentrated. Column chromatagraphy through silica gel, eluting with hexane, yielded an off-white, light weight fibrous solid: yield, 1.00 g (3.60 mmoles, 44.0%); mp 114–114.5°C; IR (KBr) 3070, 1600, 1495, 1455, 1445, 1425, 1385 and 745 cm^{-1}; MS (70 eV) m/e 278 (molecular ion); ^1H NMR ($CDCl_3$) δ 7.32–7.45 (m, 10H, phenanthryl H_2–H_8 and phenyl H_3, H_4, H_5 protons), 8.10 (s, 1H, phenanthryl H_9) and 8.45–8.90 ppm (m, 3H, phenanthryl H_1 and phenyl H_2, H_6). ^{13}C NMR ($CDCl_3$) δ 132.00, 131.90 (2), 131.44, 131.32, 130.46, 130.31, 128.70, 128.64 (2), 127.58, 127.21, 127.09, 123.61, 122.96, 122.77, 119.82, 94.18, and 88.03 ppm.

Anal. for $C_{22}H_{14}$ (278.35):

Calculated: C, 94.93; H, 5.07.
Found: C, 94.73; H, 5.07.

9-(3-Phenyl-2-propynylidene)fluorene

To a Schlenk tube charged with 3.77g (8.25 mmoles) of (3-phenyl-1,2-propadienyl)triphenylphosphonium bromide in 50 ml of anhydrous tetrahydrofuran (THF) at −78°C, was added 11.0 ml of a 1.0M solution of n-butyllithium in hexane. The mixture was stirred at −78°C for 30 min. and was treated by dropwise addition with a solution of 1.30 g (7.22 mmoles) of 9-fluorenone in 10 ml of anhydrous THF. The resulting mixture was stirred at −78°C for another 30 min and then warmed to 25°C over 1 hr.

Thin layer chromatography (silica gel plate, hexane eluant) of the reaction mixture indicated the presence of two products in addition to triphenylphosphine oxide and unreacted fluorenone. The reaction mixture was stirred for 30 hr at 25°C and then heated at reflux for 2 hr. The progress was followed by thin layer chromatography at appropriate intervals. No appreciable change from the results of the initial thin layer chromatography was apparent. The mixture was worked up by diluting with 100 ml of 10% hydrochloric acid and extracting with 3 x 50 ml of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and concentrated to an oil. Chromatographic separation through a silica gel column, eluting with hexane, gave two fractions of 200 ml each.

Fraction 1 contained 100 mg (0.455 mmoles, 6.30%) of 9-(1-butylidene)fluorene: mp 49–50°C; MS (70 eV) m/e 220 (molecular ion); ^{1}H NMR ($CDCl_3$) δ 1.05 (distorted t, 3H, J = 7.0 Hz, CH_3), 1.70 (broad sextet, 2H, J = 7.0 Hz, $-CH_2CH_2CH_3$), 2.77 (q, 2H, J = 7.0 Hz, $-CH_2CH_2CH_3$), 6.50 (t, 1H, J = 7.0 Hz, vinylic), 7.13–7.40, and 7.47–8.00 ppm (2 m's, 8H, aromatic).

Fraction 2 contained the desired 9-(3-phenyl-2-propynylidene)fluorene: 72.0 mg (0.271 mmoles, 3.75%); IR (KBr) 3060, 2180, 1620, 1600, 1490, 1445, 772, 752, 728 and 690 cm^{-1}; MS (70 eV) m/e 266 (molecular ion); 250-MHz ^{1}H NMR ($CDCl_3$) δ 6.88 (s, 1H, vinyl), 7.38–7.55 (overlapping m, 7H, fluorenyl H_2, H_3, H_6, H_7 and phenyl H_3, H_4, H_5), 7.69–7.75 (m, 2H, fluorenyl H_4, H_5), 7.74–7.85 (m, 3H, fluorenyl H_8 and phenyl H_2, H_6), and 8.66–8.74 ppm (m, 1H, fluorenyl H_1). ^{13}C NMR ($CDCl_3$) δ 144.60, 141.10, 139.72, 138.60, 137.33, 131.94, 129.56, 129.35 (2), 129.09, 128.86 (2), 127.72, 127.44, 125.25, 123.67, 120.60, 120.12, 119.98, 103.94, 101.12, and 88.96 ppm.

Phenyl-d_5-acetylene

A deaerated solution of 19.85 g (122.6 mmoles) of bromobenzene-d_5 and 18.00 g (183.7 mmoles) of ethynyltrimethylsilane in 50 ml of anhydrous triethylamine was treated with 30 mg of palladium[II] acetate and 100 mg of triphenylphosphine. The mixture was heated at 100°C under argon for 24 hr., cooled to 25°C, diluted with an equal volume of ether and filtered. The recovery of the triethylamine hydrobromide (7.418 g, 40.76 mmoles) indicated only a 33.2% conversion had been realized.

The brown filtrate was concentrated to an oil and passed through a short column of silica gel, eluting with 100 ml of hexane. The eluate was concentrated to a pale yellow oil. Distillation of the oil under reduced pressure gave two fractions. Fraction 1 (bp 40–50°C/8 torr) was recovered benzene-d_5. Fraction 2 (bp 53–60°C/1 torr) was an orange-yellow viscous oil identified as phenyl-d_5-ethynyltrimethylsilane; yield, 7.055 g (39.41 mmoles, 32.2% based on original amount of bromobenzene-d_5 or 96.7% based on % coversion); IR (film) 2980, 2300, 2175, 1270 and 870 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.20 ppm.

The silane was dissolved in 25 ml of anhydrous methanol and treated with 100 mg of anhydrous potassium carbonate. The mixture was stirred under argon at 25°C for 5 hr. The solvent was removed and the residue was taken up in 50 ml of ether and extracted with 50 ml of water. The ether portion was separated, dried over magnesium sulfate and concentrated by distilling off the solvent. The residual oil was then distilled at 1 torr into a cold trap chilled at −78°C. The yield was virtually quantitative. Identification of the product as the expected phenyl-d_5-acetylene was based on its IR (3300, 2300, 2175 cm^{-1}) and ^{1}H NMR (in $CDCl_3$, singlet at δ 3.08 ppm) spectra.

Palladium-catalyzed Reaction of 2,2'-Diiodobiphenyl with Phenyl-d_5-acetylene

A deaerated mixture of 650 mg (1.60 mmoles) of 2,2'-diiodobiphenyl, 420 mg (3.93 mmoles) of phenyl-d_5-acetylene, 10 mg of palladium[II] acetate and 50 mg of triphenylphosphine in 25 ml of anhydrous triethylamine was heated under argon at 100°C for 24 hr. The mixture was then cooled, mixed with an equal volume of ether and filtered to remove 682 mg (2.98 mmoles, 93.1% of theory) of triethylamine hydroiodide. The filtrate was concentrated and purified by column chromatography through silica gel. Fraction 1 (500 ml hexane) yielded 340 mg of crystalline 1,4-diphenylbutadiyne, mp 85–86°C. Fraction 2 (500 ml hexane) contained a trace amount of oily material which was not characterized. Fraction 3 (500 ml hexane) contained a trace quantity of a mixture and was discarded. Fraction 4 (1 liter hexane) yielded 65 mg (0.18 mmole, 11.2%) of a crystalline yellow solid, which was identified as the d_{10} analog of 3-(fluoren-9-ylidene)-1,3-diphenylpropyne: mp 114°C; IR (KBr) 3060, 2270, 2180, 1575, 1495, 785 and 730 cm^{-1}; the 250-MHz ^1H NMR spectrum showed that the splitting patterns of the protons were identical to those of the fluorenyl protons of the undeuterated compound, 3-(fluoren-9-ylidene)-1,3-diphenylpropyne. Double resonance NMR experiments performed on this deuterated compound unequivocally established the chemical shift for each and every proton on the fluorenyl skeleton (see Table 1).

Diethyl (Fluoren-9-yl)phosphonate

A mixture of 4.70 g (19.2 mmoles) of 9-bromofluorene and 3.50 g (2.11 mmoles) of triethyl phosphite was heated at 160°C for 1 hour. The oil was passed through a short silica gel column, eluting with hexane. The filtrate was evaporated to dryness to yield 3.70 g (12.3 mmoles, 64.1%) of diethyl (fluoren-9-yl)phosphonate as a colorless oil: IR (film) 3010, 1490, 1460, 1260, 1175, 1060, 1040, and 975 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (t, J = 7.0 Hz, 6H, $OCH_2\underline{CH_3}$), 2.34 (2 overlapping q's, J's = 7.0 Hz, 4H, $O\underline{CH_A}\underline{H_B}CH_3$), 4.27, 4.78 (d, 1H, $J_{P\text{-}H}$ = 31.0 Hz, fluorenyl H_9), 7.30–7.53 and 7.70–8.10 ppm (2 m's, aromatic).

Diethyl [3-(Fluoren-9-ylidene)-1,3-diphenylpropen-1-yl] Phosphate

To a slurry of 400 mg of a 50% oil dispersion of sodium hydride (8.33 mmoles) in 15 ml of anhydrous tetrahydrofuran (THF) at 0°C was added a solution of 2.00 g (6.62 mmoles) of diethyl (fluoren-9-yl)phosphonate in 10 ml of anhydrous THF. Gas evolution was instantaneous. After 30 min., a solution of 1.50 g (7.28 mmoles) of 1,3-diphenylpropynone in 10 ml of anhydrous THF was added. The mixture turned dark red and was heated at reflux for 2 hours.

The mixture was then cooled to 25°C and diluted with 100 ml of water. The yellow light weight solid was isolated by filtration and air dried. Purification by filtration through neutral alumina, followed by recrystallization from hexane, gave 3.33 g (6.56 mmoles, 99.0%) of yellow crystals of cis,trans-diethyl [3-(fluoren-9-ylidene)-1,3-diphenylpropen-1-yl] phosphate: mp 146–150°C; IR (KBr) 3080, 3000, 2940, 1605, 1580, 1460, 1070, 1040 and 780 cm^{-1}; MS (70 eV) m/e 508 (molecular ion), 354 ($M.^{+}$-$(CH_3CH_2O)_2P(O)OH$, base peak); 250-MHz ^1H NMR ($CDCl_3$) δ 1.00 (overlapping t's, 6H, O-CH_2CH_3), 3.50–4.50 (overlapping q's, 4H, O-CH_AH_B-CH_3), 6.40 (d, 1H, fluorenyl H_8), 6.80 (t x d, 1H, fluorenyl H_7), 7.00 (distorted t x d, 1H, fluorenyl H_6), 7.06–7.20, 7.25–7.40, 7.44–7.65 (3 sets of m's, 14H, phenyl protons and fluorenyl H_2,H_3,H_4,H_5), 8.17–8.27 (m, 1H, fluorenyl H_1) and 11.0 ppm (bs, 1H, hydrogen bonded vinyl H).

Anal. for $C_{32}H_{29}O_4P$ (508.53):

Calculated: C, 75.63; H, 5.75; P, 6.09.
Found: C, 75.86; H, 5.92; P, 6.27.

Thermal Decomposition of Diethyl [3-(fluoren-9-ylidene)-1,3-diphenylpropen-1-yl] Phosphate

A deaerated solution of 1.00 g (1.97 mmoles) of diethyl [3-(fluoren-9-ylidene)-1,3-diphenylpropen-1-yl] phosphate in 20 ml of N,N-dimethylacetamide was heated at 140°C for 4 hr. Thin layer chromatography (silica gel plate, 1:1 dichloromethane-hexane) showed the presence of starting material and a new yellow component.

Heating at 120°C for 100 hr did not seem to effect complete conversion, as judged by the persistent presence of the starting material on the thin layer chromatogram.

The mixture was diluted with 100 ml of water and extracted with 2 x 50 ml of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and concentrated to a brown gummy solid.

Column chromatography through silica gel, eluting with 1:4 dichloromethane-hexane, yielded 70.1 mg (0.198 mmoles, 10.1%) of 3-(fluoren-9-ylidene)-1,3-diphenylpropyne: mp 115–116°C; IR and ^1H NMR spectra were identical to those of an authentic sample.

2-Iodo-2′-(phenylethynyl)biphenyl

A deaerated slurry of 6.726 g (16.57 mmoles) of 2,2-diiodobiphenyl and 2.690 g (17.40 mmoles) of copper phenylacetylide in 100 ml of anhydrous pyridine was heated at reflux (115°C) under nitrogen. Initially, the slurry was bright yellow. After 1 hr., it became a brown

solution. The brown solution was heated for an additional 17 hr., cooled to 25°C, and diluted with an equal volume of water. The precipitate that formed was taken up in 100 ml of dichloromethane. The organic phase was separated and the blue aqueous phase was extracted twice with 50-ml portions of dichloromethane. The combined organic extracts were dried over anhydrous magnesium sulfate, filtered and evaporated to dryness.

Thin layer chromatography (silica gel plate, 1:2 dichloromethane-hexane) revealed the presence of four components. Column chromatography through a silica gel column afforded eight one-liter fractions. Fraction 1 (hexane eluant) yielded 2.022 g (4.980 mmoles, 30.1% recovery) of 2,2′-diiodobiphenyl, mp 107–108°C. Fractions 2, 3 and 4 (hexane eluant) yielded a total of 2.622 g (6.900 mmoles, 41.7%) of the desired 2-iodo-2′-(phenylethynyl)biphenyl, mp 81–82°C. Fraction 5 (hexane eluant) yielded 55 mg (0.17 mmoles, 1.0%) of 9-phenyldibenz-[a,c]anthracene, mp 231–232°C. Fraction 6 (hexane eluant) yielded 606 mg (1.71 mmoles, 10.3%) of 2,2′-bis(phenylethynyl)biphenyl, mp 118–119°C. Fractions 7 and 8 (1:2 dichloro-methane-hexane) yielded only trace amounts of impure solids and were discarded.

2-Iodo-2′-(phenylethynyl)biphenyl: mp 81–82°C; IR (KBr) 3060, 2220, 1600, 1496, 1459, 1442, 1428, 1107, 1000, 755 and 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.85–7.70 (complex m, 12H, aromatic) and 7.92, 8.05 ppm (broad d, 1H, aromatic H_3 on biphenyl unit).

Anal. for $C_{20}H_{13}I$ (380.23):

Calculated: C, 63.18; H, 3.45; I, 33.38.
Found: C, 63.00; H, 3.53; I, 33.11.

9-Phenyldibenz[a,c]anthracene: mp 231–232°C (lit. 235–236°C); IR (KBr) weak absorptions at 3060, 1600, 1490, 1445, 1365, intense absorptions at 760, 720 and 705 cm^{-1}.

Anal. for $C_{28}H_{18}$ (354.45):

Calculated C, 94.88; H, 5.12.
Found: C, 94.61; H, 5.22.

2,2′-Bis(phenylethynyl)biphenyl: mp 118–119°C; IR (KBr) 3060, 2220 (weak), 1600, 1495, 1440, 755 (intense) and 690 cm^{-1} (intense); 250-MHz ^1H NMR ($CDCl_3$) δ 7.22 (bs, 10H, H's on pendent phenyls), 7.37–7.41 (m, 4H, biphenylyl H_4,$H_{4'}$,H_5,$H_{5'}$), 7.52–7.56 (m, 2H,biphenylyl H_6,$H_{6'}$), and 7.63–7.65 ppm (m, 2H, biphenylyl H_3,$H_{3'}$); ^{13}C NMR ($CDCl_3$) δ 143.41, 132.19, 131.55 (2), 130.52, 128.35 (2), 128.17, 127.85, 127.61, 123.73, 123.08, 92.74, and 89.36 ppm.

Anal. for $C_{28}H_{18}$ (354.45):

Calculated: C, 94.88; H, 5.12.
Found: C, 95.19; H, 5.27.

Palladium-catalyzed Phenylethynylation of 2-Iodo-2′-(phenylethynyl)biphenyl

A pale yellow solution of 800 mg (2.11 mmoles) of 2-iodo-2′-(phenylethynyl)biphenyl and 235 mg (2.30 mmoles) of freshly distilled phenylacetylene in 13 ml of deaerated anhydrous triethylamine (Fluka reagent grade) was stirred at 25°C under nitrogen while 20 mg of triphenylphosphine and 10 mg of tetrakis(triphenylphosphine)palladium[0] were added. The mixture was stirred for another 5 min. and then heated to 100°C over 15 min. After 1 hour at 100°C, a copious white precipitate was obtained and the supernatant solution became bright yellow. The slurry was cooled to 25°C under argon and filtered to remove 390 mg of triethylamine hydroiodide. On chilling, the filtrate yielded a second crop of the hydroiodide (40 mg).

The filtrate was evaporated to dryness, leaving a yellow solid mass. Thin layer chromatography on silica gel indicated the presence of one yellow component. The solid in hexane was passed through a short silica gel column and recrystallized twice from hexane. Yield, 710 mg (2.01 mmoles, 95.1%): mp 115–116°C; the IR and ^{1}H NMR spectra were identical to those of authentic 3-(fluoren-9-ylidene)-1,3-diphenylpropyne.

Reaction of 2,2′-Diiodobiphenyl with One Equivalent of Phenylacetylene under Palladium Catalysis

A pale yellow solution of 4.063 g (10.00 mmoles) of 2,2′-diiodobiphenyl and 1.020 g (10.00 mmoles) of freshly distilled phenyacetylene in 100 ml of deaerated anhydrous triethylamine (Fluka reagent grade) was warmed to 50°C under argon. The catalyst (50 mg of triphenylphosphine and 20 mg of palladium[II] acetate) was added. The mixture was brought to 90°C over 15 min. Precipitation commenced and the reaction mixture was stirred at 90°C for 21 hr. The slurry was cooled under argon and diluted with 100 ml of ether. The white insoluble triethylamine hydroiodide was filtered off (2.12 g, 92.5% recovery). The orange yellow filtrate was concentrated, and dissolved in 200 ml of ether. The organic solution was washed with 200 ml of 10% aqueous hydrochloric acid, 200 ml of saturated sodium bicarbonate and then with water. After drying over anhydrous magnesium sulfate, the solution was concentrated.

High performance liquid chromatography of the crude product indicated the presence of 2,2′-diiodobiphenyl (44.9%), 3-(fluoren-9-ylidene)-1,3-diphenylpropyne (44.3%) and a third component (ca. 10.8%).

Column chromatography (silica gel) of the crude product mixture yielded three fractions. Fraction 1 (hexane eluant) was found to contain 1.784 g (4.394 mmoles, 43.9% recovery) of 2,2'-diiodobiphenyl (mp 108–109°C). Fraction 2 (hexane eluant) contained a trace amount of an oil which was not characterized. Fraction 3 (1:4 dichloromethane-hexane eluant) contained 1.021 g (2.88 mmoles, 28.8% isolated yield) of 3-(fluoren-9-ylidene)-1,3-diphenylpropyne, which was identified by its mp (115–116°C) and mixed mp with an authentic sample.

Reaction of 2-Iodo-2'-(phenylethynyl)biphenyl with Tetrakis(triphenylphosphine)palladium[0] in Triethylamine at Reflux

A brownish yellow slurry of 381 mg (1.00 mmole) of 1-iodo-2'-(phenylethynyl)biphenyl and 1.152 g (0.998 mmole) of tetrakis(triphenylphosphine)palladium[0] in 13 ml of deaerated anhydrous triethylamine was heated at a gentle reflux (oil bath at 100°C) under nitrogen for 1.5 hr. The solid in the slurry appeared to be more copious and lighter yellow in color than at the start. The mixture was cooled, diluted with 50 ml of ether, and filtered to give a yellow powdery solid.

The yellow orange filtrate was evaporated to dryness to give a solid mass. Thin layer chromatography (silica gel plate) indicated triphenylphosphine was the predominant component. Several other components were present in trace quantities.

The yellow powdery solid isolated from the reaction was identified as iodo(fluoren-9-ylidenebenzyl)bis(triphenylphosphine)palladium[II]: yield, 981 mg (0.970 mmole, 97.2%); mp 204–206°C; IR (KBr) 3050, 1570, 1481, 1435, 1085, 780, 740, 730 and 690 cm^{-1}; 250-MHz ^1H NMR ($CDCl_3$) δ 6.36(d, 1H, J=7.5 Hz, fluorenyl H_8), 6.48 (broad d, 2H, J=7.5 Hz fluorenyl H_2, H_7), 6.65 (d x d x d, 1H, J=7.5, 7.5, 1.0 Hz, fluorenyl H_6), 6.84–7.67 (3 sets of multiplets, 38H, fluorenyl H_3, H_4, H_5, and all phenyl H's), and 9.83–9.87 ppm (m, 1H, fluorenyl H_1).

Anal. for $C_{56}H_{43}IP_2Pd$ (1011.16):

Calculated: C, 66.52; H, 4.29; I, 12.55.
Found: C, 66.39; H, 4.29; I, 12.67.

Reaction of Phenylacetylene with Iodo(fluoren-9-ylidenebenzyl)bis(triphenylphosphine)palladium[II].

A mixture of 401 mg (0.397 mmole) of iodo(fluoren-9-ylidenebenzyl)bis(triphenylphosphine)palladium[II] and 55 mg (0.54 mmole) of phenylacetylene in 10 ml of deaerated, anhydrous triethylamine (Fluka reagent grade) was heated at 100°C under nitrogen for 10 min. At this point, the yellow complex turned black.

The mixture was cooled, diluted with 50 ml of ether and filtered. Unreacted starting yellow complex was isolated (214 mg; i.e., the reaction was ca. 50% over in 10 minutes).

The black filtrate was concentrated to give a brown mass. Thin layer chromatography (silica gel plate) indicated the presence of bright yellow 3-(fluoren-9-ylidene)-1,3-diphenylpropyne. Column chromatography through silica gel, eluting with 1:4 dichloromethane-hexane (1 liter), removed a bright yellow band. Evaporation of the eluate to dryness, followed by recrystallization of the solid from hexane, gave bright yellow crystals of 3-(fluoren-9-ylidene)-1,3-diphenylpropyne: Yield, 30 mg (0.085 mmoles, 21%); mp 114–116°C; IR and ^{1}H NMR spectra were identical to those of an authentic sample.

Reaction of Iodine with Iodo(fluoren-9-ylidenebenzyl)bis(triphenylphosphine)palladium[II].

A solution of 204 mg (0.202 mmoles) of iodo(fluoren-9-ylidenebenzyl)bis(triphenylphosphine)palladium[II] in 50 ml anhydrous dichloromethane was treated by dropwise addition with a 0.134 N solution of iodine in dichloromethane (standaridized against sodium thiosulfate). At the end point, the purple color of iodine persisted. The mixture was then diluted with an equal volume of hexane and filtered to remove the orange-yellow diiodobis-(triphenylphosphine)palladium[II] complex: mp 263–264°C.

The filtrate was concentrated. Thin layer chromatography on a silica gel plate indicated the presence of (α-iodobenzylidene)fluorene. Column chromatography through silica gel, eluting with hexane, yielded analytically pure needles of (α-iodobenzylidene)fluorene:11.5 mg (0.030 mmoles, 15.0 %), mp. 137–138°C; IR (KBr) 3050, 1610, 1580, 1572, 1445 (strong), 940, 776 (strong), 758, 728 (very strong), and 692 cm^{-1}; GC-MS indicated 99+% purity and a molecular ion at m/e 380; 250-MHz ^{1}H NMR ($CDCl_3$) δ 6.09 (d x d, 1H, J's = 8.2, 0.8 Hz, fluorenyl H_8), 6.81 (d x d x d, 1H, J's = 8.2, 8.2, 0.8 Hz, fluorenyl H_7), 7.21 (d x d x d, 1H, J's = 8.2, 7.5, 0.8 Hz, fluorenyl H_6), 7.63 (d x d, 1H, J's = 7.5, 0.8 Hz, fluorenyl H_5), 7.71 (m, 1H,fluorenyl H_4), 7.33–7.73 (complex m, 7H, fluorenyl H_2, H_3 and phenyl H's), and 9.04–9.08 ppm (m, 1H, fluorenyl H_1); ^{13}C NMR ($CDCl_3$) δ 147.84, 142.03, 141.06, 139.68, 138.82, 138.41, 129.73, 129.38, 128.96, 128.46, 127.86, 127.16, 126.67, 125.54, 125.04, 119.80, 119.19, and 99.46 ppm.

Anal. for $C_{20}H_{13}I$ (380.23):

Calculated: C, 63.18; H, 3.45; I, 33.38
Found: C, 63.25; H, 3.34; I, 33.45

2,2'-Bis(phenylethynyl)-5,5'-diaminobiphenyl

A mixture of 0.700 g (1.58 mmoles) of 2,2'-bis(phenylethynyl)-5,5'-dinitrobiphenyl and 0.225 g of 5% ruthenium-on-charcoal in 150 ml of 2-propanol was hydrogenated under 4

atmospheres of hydrogen for 20 hr at 25°C. The mixture was filtered through Celite and washed with chloroform. After evaporation of the solvents, the light weight yellow solid was recrystallized from dichloromethane-hexane, mp 158–160°C; IR (KBr) 3390 (strong, broad), 2220 (weak), 1620, 1590, 1500 cm $^{-1}$ (strong, sharp); MS (70 eV) m/e 384 (molecular ion); ^{1}H NMR ($CDCl_3$) δ 3.68 (bs, 2H, $N\underline{H}_2$), 6.68 (d x d, 1H, aromatic C_4 proton, $J_{3,4}$ = 8 Hz, $J_{4,6}$ = 2 Hz), 6.85 (d, 1H, aromatic C_6 proton, $J_{4,6}$ = 2 Hz), 7.25 (s, 5H, phenyl) and 7.50 ppm (d, 1H, aromatic C_3 proton, $J_{3,4}$ = 8 Hz).

1,3-Diphenylpropynone Anil

N-Phenylbenzimidoyl chloride was prepared by treatment of N-phenylbenzamide with phosphorus pentachloride in 90% yield; bp 120–125°C/0.1 torr and mp 40–40.5°C. A solution of 21.5 g (100 mmoles) of N-phenylbenzimidoyl chloride in 250 ml of deaerated triethylamine was treated with 11.2 g (110 mmoles) of phenylacetylene, 0.1 g of palladium[II] acetate and then with 0.2 g of triphenylphosphine. The mixture was heated to 80°C and kept at 80°C for 2 hrs. After cooling, diluting with an equal volume of ether, and filtering, 10.5 g of triethylamine hydrochloride was isolated (98% of theory). The filtrate was concentrated and eluted through a short column of silica gel with hexane. The eluate was concentrated to yield yellow rhombic crystals: 27.5 g (98 mmoles, 98.0%); mp 60.5–61°C; IR (KBr) 2200 (intense), 1560, 1495, 1450, 1320, 1195, 755, 690 cm^{-1}; MS (70 eV) m/e 281 (molecular ion); NMR ($CDCl_3$) δ 7.00–7.68 (m, 8H, aromatic), 7.30 (s, 5H, 3-phenyl) and 8.18–8.45 ppm (m, 2H, ortho H's on 1-phenyl).

Propiolophenone Anil and Its Precursor 3-(Trimethylsilyl)propiolophenone Anil

A solution of 21.5 g (0.100 mole) of N-phenylbenzimidoyl chloride in 250 ml of deaerated triethylamine was treated with 10.5 g of ethynyltrimethylsilane, with 0.1 g of palladium[II] acetate, and then with 0.2 g of triphenylphosphine. The mixture was slowly heated to 80°C and kept at 80°C for 2 hr. After cooling, diluting with an equal volume of ether, and filtering, 10.5 g of triethylamine hydrochloride was isolated (98% of theory). The filtrate was concentrated and eluted through a short column of silica gel with hexane. The eluate was concentrated and distilled at 130–135°C/0.1 torr to yield a viscous yellow oil which was identified as 3-(trimethylsilyl)propiolophenone anil: 21.7 g (78.3 mmoles, 78.3%); IR (film) 3080, 2990, 2160 (weak), 1590, 1565, 1490, 1455, 1280, 1260, 1215, 1050, 1030, 850 cm^{-1}; MS (70 eV) m/e 277 (molecular ion); NMR ($CDCl_3$) δ 0.12 (s, 9H, $SiC\underline{H}_3$), 6.95–7.50 (m, 8H, N-Ph and aromatic H_3, H_4, H_5), and 8.10–8.30 ppm (m, 2H, aromatic H_2 and H_6).

Anal. for $C_{18}H_{19}NSi$ (277.44):

Calculated: C, 77.93; H, 6.90; N, 5.05; Si, 10.12.
Found: C, 78.01; H, 6.88; N, 4.85; Si, 10.38.

To a solution of 1.50 g (5.42 mmole) of 3-(trimethylsilyl)propiolophenone anil in 10 ml of anhydrous methanol was added 100 mg of anhydrous potassium carbonate. Immediately an exothermic reaction took place, and a copious crystalline precipitate was formed. The mixture was filtered and the crystalline pale yellow solid was washed with cold methanol: 1.00 g (4.88 mmole, 90.0%); mp 117–117.5°C; IR (KBr) 3220 (intense), 2080 (intense), 1590, 1580, 1455, 1380 cm^{-1}; MS (70 eV) m/e 205 (molecular ion); NMR ($CDCl_3$) δ 3.28 (s, 1H, C=CH), 6.95–7.50 (m, 8H, N-Ph and aromatic H_3, H_4, H_5) and 8.10–8.30 ppm (m, 2H, aromatic H_2, H_6).

Anal. for $C_{15}H_{11}N$ (205.26):

Calculated: C, 87.77; H, 5.40; N, 6.82.
Found: C, 87.81; H, 5.50; N, 6.83.

2-(Phenylethynyl)benzaldehyde

A mixture of 3.70 g (20.0 mmoles) of 2-bromobenzaldehyde and 2.55 g (25.0 mmoles) of phenylacetylene in 50 ml of deaerated, anhydrous triethylamine was stirred at 25°C under nitrogen as 58.2 mg (0.259 mmole) of palladium[II] acetate and 121.6 mg (0.464 mmole) of triphenylphosphine were added. The mixture was clear yellow. Upon heating slowly to 80°C (over 45 minutes), the color of the medium turned orange and a copious white precipitate was formed. The mixture was heated at 80°C for an additional hour.

The cooled mixture was mixed with an equal volume of hexane, filtered, and washed thoroughly with hexane. The yield of triethylamine hydrobromide was 3.59 g (19.7 mmoles, 98.6%). Thin-layer chromatography (silica gel, 1:2 dichloromethane-hexane) revealed the presence of 1,4-diphenyl-1,3-butadiyne and a fluorescent product.

Silica gel column chromatography separated the Glaser product (white needles, mp 85°C) in the hexane eluate. Elution with 20% dichloromethane in hexane followed by distillation at 139–141°C/0.15 torr yielded 2-(phenylethynyl)benzaldehyde: 3.60 g (17.5 mmoles, 87.4%); IR (KBr) 2840, 2740, 2220, 1690 cm^{-1} (intense): MS (70 eV) m/e 206 (molecular ion); NMR ($CDCl_3$) δ 7.18–7.65 (m, 8H, aromatic), 7.78–8.00 (m, 1H, ortho H) and 10.62 ppm (s, 1H, CHO).

Anal. for $C_{15}H_{10}O$ (206.24):

Calculated: C, 87.36; H, 4.89
Found: C, 87.20; H, 4.95.

The alternative metal catalyst system used to effect coupling between 2-bromobenzaldehyde and phenylacetylene was dichlorobis(triphenylphosphine)palladium[II], copper[I] iodide in triethylamine (Reference 26). The reaction was incomplete after 17 hours at 65°C. The method was considered inferior to the Heck procedure (Reference 25).

trans-(2-Phenylethynyl)stilbene

The literature procedure (Reference 124) was adopted. The Wittig reagent was prepared by treatment of 9.99 g (25.7 mmoles) of benzyltriphenylphosphonium chloride in anhydrous ether with 29.5 ml of a 0.96M hexane solution of n-butyllithium under nitrogen at 0°C. The orange-colored ylide was stirred at 25°C for 1 hour and treated with 5.23 g (25.4 mmoles) of 2-(phenylethynyl)benzaldehyde. The resulting mixture was stirred at 25°C for 16 hrs, diluted with 130 ml of hexane and filtered. The filtrate was concentrated and was shown by thin-layer chromatography (silica gel, 1 : 2 dichloromethane-hexane) to contain a fluorescent product as the only component. Purification by column chromatography on silica gel, eluting with hexane, yielded 831 mg (2.97 mmoles, 11.7%) of crystalline product: mp 94–94.5°C; IR (KBr) 2200, 1590, 1490, 965 cm^{-1}; MS (70 eV) m/e 280 (molecular ion).

2-(Phenylethynyl)benzaldehyde Anil

Upon mixing 13.6 g (66.0 mmoles) of 2-(phenylethynyl)benzaldehyde and 6.25 g (67.2 mmoles) of distilled aniline, a yellow precipitate formed instantaneously with slight heat formation. The mixture was treated with 100 ml of hexane and 1 g of magnesium sulfate and was heated at reflux for 1 hr. Filtered while hot, the yellow solution was evaporated down to half of the original volume, cooled to 25°C and then chilled at −78°C. The white solid which separated was isolated by filtration, redissolved in hexane, treated with charcoal and recrystallized. The purified product obtained in 2 crops weighed 14.1 g (50.2 mmoles, 76.0%); mp 63–64°C; IR (KBr) 2200, 1620, 1580, 1490 cm^{-1}; MS (70 eV) m/e 281 (molecular ion), 204, 104; ^1H NMR ($CDCl_3$) δ 7.20–7.60 (m, 13H, aromatic), 8.3 (m, 1H, ortho H), and 9.10 ppm (s, 1H, CH).

Anal. for $C_{21}H_{15}N$ (281.36):

Calculated: C, 89.65; H, 5.37; N, 4.98.
Found: C, 89.28; H, 5.14; N, 5.14.

N-Benzylidene-2-iodoaniline

A mixture of 21.9 g (100 mmoles) of iodoaniline and 10.6 g (100 mmoles) of benzaldehyde was heated without a solvent at 80°C for 3.5 hr. The gummy purple mixture was mixed with hot hexane and the supernatant was decanted. Upon cooling to −78°C, the hexane supernatant yielded a white precipitate: yield, 23.6 g (76.9 mmoles, 76.9%); mp 57–57.5°C [lit. (Reference 125): mp 57.5°C; IR (KBr) 1620, 1570 cm^{-1}; MS (70 eV) m/e 307 (molecular ion), 180.

N-Benzylidene-2-aminotolane

A mixture of 5.65 g (18.4 mmoles) of N-benzylidene-2-iodoaniline and 1.88 g (18.5 mmoles) of phenylacetylene in 30 ml of deaerated, anhydrous triethylamine was stirred at 25°C under nitrogen as 18.0 mg of dichlorobis(triphenylphosphine)palladium[II] and 21.8 mg of copper[I] iodide were added. After 3 hrs, the mixture was filtered to remove triethylamine hydroiodide (3.91 g, 92.7%). The filtrate was concentrated and pumped at 0.1 torr to remove the last trace of triethylamine. The yellow oil was mixed with 1 : 5 dichloromethane-hexane, treated with 1 g of charcoal and filtered through Celite. Upon cooling to −78°C the filtrate yielded a pale yellow crispy solid: 3.30 g (11.7 mmoles, 63.8%); mp 64–65°C; IR (KBr) shows the absence of NH absorptions and a strong imine band at 1625 cm^{-1}; MS (70 eV) m/e 281 (molecular ion), 204, 194, 193, 181.

The imine product was extremely sensitive hydrolytically. Attempts to purify the product by column chromatography using silica gel, Florisil (15% magnesium oxide in silica), basified silica gel and neutral Woelm alumina resulted in the isolation of benzaldehyde and white needles of 2-aminotolane (mp 91–92°C).

Column chromatography of the crude imine product through cellulose provided a method for purification. The pale yellow crystals obtained had mp 66–67°C.

Formation of 4b,5-Dihydro-10-phenylindeno[1,2-b]indole. Thermal Intramolecular Cyclization of N-Benzylidene-2-Aminotolane

A solution of 1.00 g (3.56 mmoles) of N-benzylidene-2-aminotolane in 3.0 g of deaerated tetralin was heated under nitrogen at 150–160°C for 6 hrs. Silica gel thin-layer chromatography was used to monitor the progress of the reaction. At the end of the heating period,

TLC indicated total disappearance of the starting imine and the presence of one major component.

The crude, dark brown oil was purified by column chromatography on silica gel. Elution with hexane removed tetralin. Elution with 20–50% dichloromethane in hexane yielded a white granular solid: 233 mg (0.829 mmoles, 23.3%); mp 264°C; IR (KBr) 3420, 1600, 1490, 1450 cm $^{-1}$; MS (70 eV) m/e 281 (molecular ion); ^{1}H NMR ($CDCl_3$) δ 6.10 (s, 1H, methine), 6.80–7.50 (m, 13H, aromatic) and 8.00 ppm (broad s, 1H, NH).

Anal. for C_{21} H_{15} N (281.36):

Calculated: C, 89.65; H, 5.37; N, 4.98.
Found: C, 89.28; H, 5.42; N, 5.56.

Formation of 4b,5-Dihydro-5-phenylindeno[1,2-b]indole. Thermal Intramolecular Cyclization of 2-(Phenylethynyl)benzaldehyde Anil.

A solution of 4.00 g (14.2 mmoles) of 2-(phenylethynyl)benzaldehyde anil in 10.0 g of tetralin was deaerated by bubbling nitrogen through and then it was heated under nitrogen at 175° for 7 hours. The progress of the reaction was followed by hourly silica gel thin-layer chromatography (1:2 dichloromethane-hexane). The mixture was cooled to room temperature and taken up in 100 ml of hexane. An off-white precipitate was obtained and decolorized with charcoal: yield 772 mg (2.75 mmoles, 19.3%); mp 277–281°C (dec); IR (KBr) 1590, 1490, 1240 cm^{-1}; MS (70 eV) m/e 281 (molecular ion).

Thermal Intramolecular Cyclization of 2-(Phenylethynyl)benzaldehyde Anil in Diphenyl Ether Solvent

A solution of 2.90 g (10.3 mmoles) of 2-(phenylethynyl)benzaldehyde anil in 15 ml of diphenyl ether was thoroughly deaerated with argon and then rapidly heated to 210°C (over 5 min) under argon. The solution turned dark brown. After 2 hr at 210°C, the disappearance of the starting material was complete as determined by silica gel thin-layer chromatography. The mixture was cooled to 50°C and diluted with 100 ml of diethyl ether to cause a white precipitate to form. Purification by silica gel column chromatography, eluting with 1:1 dichloromethane-hexane, yielded a white powdery product: mp 295–297°C (decomp.); IR (KBr) 3080, 1605 (intense), 1500 (intense), 1465, 1350, 1250, 755 cm^{-1}; MS (70 eV) m/e 487 (molecular ion, base peak), 358, 282, 204; ^{1}H NMR (DMSO-d_6) δ 6.82, 7.30, 7.75 ppm (3 complex m, aromatic).

(3-Phenyl-1,2-propadienyl)triphenylphosphonium Bromide

A mixture of 10.4 g (53.5 mmoles) of 3-phenylpropargyl bromide and 18.3 g (69.6 mmoles) of triphenylphosphine in 150 ml of toluene was heated at reflux under nitrogen for 4 hrs. The mixture was then cooled and the precipitate collected and air-dried for 18 hrs: yield, 22.5 g (49.2 mmoles, 92.0%); mp 212°C; IR (KBr) 1930 (allene), 1440, 1110 cm^{-1}.

trans-1-[2-(Phenylethynyl)phenyl]-4-phenylbuta-1-en-3-yne

A suspension of 7.30 g (16.0 mmoles) of 3-phenyl-1,2-propadienyltriphenylphosphonium bromide in 50 ml of anhydrous tetrahydrofuran was treated at 0°C under nitrogen with 14.8 ml of a 1.15 M solution of n-butyllithium in hexane. A deep red mixture was obtained and stirred at 25°C for 2 hrs before being treated with 3.05 g (15.0 mmoles) of 2-(phenylethynyl)-benzaldehyde at 25°C. The solution was stirred at 25°C for 20 hrs, poured into 100 ml of water and extracted three times with 100-ml portions of dichloromethane. The organic extracts were combined, washed with 100 ml of water, dried over anhydrous magnesium sulfate and concentrated to a brown oil. Silica gel thin-layer chromatography (1:2 dichloromethane-hexane) showed the complete absence of the aldehyde and the appearance of one fluorescent product with a high R_f. Silica gel column chromatography, eluting with hexane, removed a yellow oil which was treated once with charcoal, yielding 3.46 g of oil(11.4 mmoles, 75.4%); IR (neat) 2220, 2180, 1600, 1490, 1440, 955 cm^{-1}.

Thermal Cyclization of trans-1-[2-(Phenylethynyl)phenyl]-4-phenylbuta-1-en-3-yne

A mixture of 3.46 g (11.4 mmoles) of trans-1-[2-(Phenylethynyl)phenyl]-4-phenylbuta-1-en-3-yne in 9.7 g of tetralin was deaerated and heated at 175°C under nitrogen for 4 hrs. The progress of reaction was monitored by hourly silica gel thin-layer chromatography. As no apparent changes took place, the mixture was heated at reflux (207°C) for 43 hrs. Thin-layer chromatography (silica gel, 1:4 dichloromethane-hexane) indicated still no noticeable change.

Silica gel column chromatography, eluting with hexane, separated tetralin and the starting material (identifiable by IR spectroscopy). Upon standing, the end fraction of tetralin deposited a crystalline material which was isolated by filtration and washing with cold hexane: yield, 118 mg (0.388 mmoles, 3.40%); mp 192–193°C; IR (KBr) no C=C band at 1600, weak absorptions at 1500, 1370, 890 cm^{-1}; MS (70 eV) m/e 304 (molecular ion), no other fragments were observed.

Thermal Cis-Trans Isomerization of (Z)-2,α'-Bis(phenylethynyl)stilbene (Attempted Thermal Cyclization)

The starting material was synthesized (Reference 123) via a conventional palladium-catalyzed reaction between (Z)-2,α'-dibromostilbene and phenylacetylene in 20% yield (unoptimized): mp 85–86°C; IR (KBr) 1600, 1495, 1450 cm^{-1} (Note: This spectrum does not resemble that of 1,4-diphenyl-1,3-butadiyne); MS (70 eV) m/e 380 (molecular ion).

A solution of 514 mg (1.36 mmoles) of (Z)-2,α'-bis(phenylethynyl)stilbene in 1.30 g of deaerated tetralin was heated under nitrogen at 175°C for 24 hrs. The progress of reaction was monitored by silica gel thin-layer chromatography at convenient intervals. As TLC did not indicate appreciable change, the mixture was heated at reflux (207°C) for 24 hrs. Still no appreciable change was noticeable on TLC. The mixture was purified by silica gel column chromatography.

The first hexane eluate contained only tetralin. Subsequent elution isolated a yellow solid which was treated with charcoal and recrystallized from petroleum ether: yield, 250 mg (29.0%); mp 182–184°C; IR (KBr) 1600, 1495, 1450, 900 cm^{-1}; MS (70 eV) m/e 380 (molecular ion); ^1H NMR ($CDCl_3$) δ 7.10–8.00 (m, 19H, aromatic) and 8.40 ppm (s, 1H, vinylic).

1,4-Dibromo-1,2,3,4-tetraphenylbutadiene

The lithium reagent 1,4-dilithio-1,2,3,4-tetraphenylbutadiene was prepared according to Reference 127. The mixture of 4.42 g (24.8 mmoles) of diphenylacetylene and 0.172 g (24.8 mmoles) of cut lithium wire was stirred under nitrogen in 50 ml of absolute ether at room temperature. A red color developed after 30 minutes. After 15 hrs, the mixture was mixed with 50 ml of tetrahydrofuran (THF) to give a green solution of the dilithio reagent.

A 2-ml aliquot of the green solution was removed and treated with 10 ml of anhydrous ethanol to give a 70% yield of 1,2,3,4-tetraphenylbutadiene: mp 183–184°C (lit. 183–185°C); IR (KBr) 3080, 1605, 1500, 1450, 760, 700 cm^{-1}; MS (70 eV) m/e 358 (molecular ion); 1_H NMR ($CDCl_3$) δ 6.38 (s, 2H, vinyl H), 6.66–7.45 (m, 10H, inner phenyls) and 7.34 ppm (distorted s, 10H, terminal phenyls).

The green solution was cooled to −78°C and a 20-ml THF solution of 8.23 g (24.8 mmoles) of carbon tetrabromide was added. The resulting mixture was stirred at room temperature for 1 hr, poured into 300 ml of water and the phases were separated. The aqueous layer was extracted three times with 200-ml portions of ether. All organic fractions were combined, dried over anhydrous magnesium sulfate and concentrated to a brown oil. Silica gel column chromatography, eluting with hexane, separated 0.955 g of unreacted carbon tetrabromide. Elution with 10% dichloromethane in hexane yielded 4.16 g (8.06 mmoles, 65.0%) of 1,4-dibromo-1,2,3,4-tetraphenylbutadiene: mp 148–148.5°C; IR (KBr) 1590, 1480, 1435 cm^{-1}; MS (70 eV) m/e 518, 516, 514 (molecular ion), 437, 435 (loss of 1 Br).

1-Bromo-2-phenylacetylene

To 800 ml of water were added 300 g of sodium hydroxide and 10 g of stearic acid. The solution was cooled to 0°C and 160 g (1.00 mole) of bromine was added rapidly with stirring. The mixture was then treated with 87.0 g (0.853 mole) of phenylacetylene to give a thick emulsion. After vigorous stirring for 2 hrs at 25°C, the reaction flask was immersed in a 60°C water bath for 1.5 hrs, cooled to 25°C and the contents were transferred to a separatory funnel. The reaction mixture was then extracted with 3 × 500 ml of ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate and concentrated to a dark brown oil. Distillation at 30–50°C/0.1 torr removed 30 g of a forecut that was shown by IR and NMR to be mainly phenylacetylene. The desired product was finally distilled at 55–60°C/0.01 torr: 39.5 g (0.218 mole, 25.6%); IR (film) 2210 (weak), 1660, 1490, 1445, 750 cm^{-1}; ^1H NMR ($CDCl_3$) showed only aromatic multiplets.

Reaction between 1-Bromo-2-phenylacetylene and 1,4-Dilithio-1,2,3,4-tetraphenylbutadiene

The dilithio compound was prepared by treatment of 0.52 g of lithium wire with 13.4 g (75 mmoles) of diphenylacetylene in 60 ml of absolute ether at 25°C. After 17 hr, the slurry was mixed with 200 ml of anhydrous tetrahydrofuran (THF) to obtain a dark green solution. The solution was cooled to −78°C and treated with 13.5 g (75 mmoles) of 1-bromo-2-phenylacetylene. A yellow precipitate was formed instantaneously. The mixture was allowed to warm up to 25°C over 2 hr. At 25°C, a yellow brown solution resulted, which was treated with 50 ml of methanol and extracted in succession with 200 ml each of saturated sodium chloride solution and water. After drying and concentrating, the brown oil was eluted through a silica gel column with dichloromethane-hexane. The initial hexane fractions contained mixtures of phenylacetylene, bromophenylacetylene and diphenylacetylene. The 1:1 dichloromethane-hexane eluate yielded 7.45 g (14.5 mmoles) of white crystals identified as 1,4-dibromo-1,2,3,4-tetraphenylbutadiene: mp 145–147°C; IR (KBr) 1590, 1480, 1435 cm^{-1}; MS (70 eV) m/e 518, 516, 514 (molecular ions).

Anal. for $C_{28}H_{20}Br_2$ (516.29):

Calculated: C, 65.14; H, 3.90; Br, 30.96.
Found: C, 65.04; H, 3.92; Br, 30.92.

The yield of the dibromo compound was 38% of theory.

Attempted Reaction between Bromo(phenylethynyl)bis(triphenylphosphine)palladium[II] and 1,4-Dilithio-1,2,3,4-tetraphenylbutadiene

Bromo(phenylethynyl)bis(triphenylphosphine)palladium[II] was prepared by mixing 1-bromo-2-phenylacetylene and tetrakis(triphenylphosphine)palladium[0] in benzene at 25°C. The IR spectrum and the elemental analysis were consistent with the proposed structure.

A tetrahydrofuran solution of 4 g of the palladium[II] complex was treated under argon with 2.5 mmoles of dilithiotetraphenylbutadiene. An immediate reaction occurred and the solution turned very dark brown. After solvent removal, the residue was examined by thin-layer chromatography and shown to contain a multitude of components. Further work was abandoned.

Attempted Reaction between 1,4-Dilithio-1,2,3,4-tetraphenylbutadiene and Phenylacetyl Chloride

A suspension of 1.1 g (0.16 mole) of lithium wire in 150 ml of anhydrous ether containing 26.8 g (0.151 mole) of diphenylacetylene was stirred under argon at 20°C for 17 hr. The characteristic yellow precipitate of dilithiotetraphenylbutadiene was formed. The slurry was mixed with an equal volume of deaerated anhydrous tetrahydrofuran (THF) to yield a dark green solution. Under argon, the green solution was cooled to −78°C and treated with 23.5 g (0.152 mole) of phenylacetyl chloride in 50 ml of THF. Immediately, the dark green color faded to a yellow tint and a copious precipitate was obtained. The slurry was stirred at −78°C for 1.5 hr and then at 25°C for 1 hr.

After hydrolysis in 1.5 liters of water, the organic solvent was allowed to evaporate and the aqueous slurry was filtered to give an off-white solid which was dissolved in 200 ml of ether; this solution was extracted with 100 ml of 10% sodium hydroxide, washed with 100 ml of water and dried over anhydrous magnesium sulfate. After solvent removal, the residue was recrystallized from hexane-ether to yield 8.75 gm (24.6 mmoles, 32.6%) of 1,2,3,4-tetraphenylbutadiene: mp 183–184°C; IR (KBr) 3080, 1605, 1500, 1450, 760, 700 cm^{-1}; MS (70 eV) m/e 358 (molecular ion); ^1H NMR ($CDCl_3$) δ 6.38 (s, 2H, vinyl H), 6.66–7.45 (m, 10H, inner phenyls) and 7.34 ppm (distorted s, 10H, terminal phenyls).

The aqueous phase left behind was acidified and extracted with 3 × 100 ml of ether. The combined ethereal fractions were washed with 100 ml of water, dried over anhydrous magnesium sulfate and concentrated to a white solid. It was identified as phenylacetic acid: 1_H NMR ($CDCl_3$) δ 3.57 (s, 2H, $C\underline{H}_2$ Ph), 7.27 (s, 5H, aromatic) and 10.60 ppm (bs, 1H, CO_2H).

N-Benzoyl-2-iodoaniline and N-(2-Iodophenyl)benzimidoyl Chloride

A dispersion of 25.0 g (114 mmoles) of 2-iodoaniline in 300 ml of water was stirred at 25°C and treated with 18.0 g (128 mmoles) of benzoyl chloride. The mixture was heated at 75–80°C for 1 hr, cooled to 25°C and treated with 50 ml of 20% aqueous sodium hydroxide. The white solid was filtered off and washed with 100 ml each of 10% aqueous sodium hydroxide and water. The crude solid was recrystallized from a 3:1 ethanol-toluene solvent system to yield fluffy white crystals: 25.6 g (79.3 mmoles, 69.5%); mp 137–138°C; IR (KBr) 3340 (intense), 1710 (intense), 1560, 1510, 1335 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.66–8.60 (complex m, 9H, aromatic) and 8.30 ppm (broad s, 1H, NH).

A mixture of the benzamide product (15.1 g, 46.7 mmoles) above and phosphorus pentachloride (10.5 g, 50.4 mmoles) was heated under argon at 100°C for 30 min. The phosphorus oxychloride generated was removed by distillation at 20–25 torr. The residue was distilled at 140–145°C/0.1 torr to give 14.0 g (41.0 mmoles, 87.8%) of the imidoyl chloride product: IR (film) 3080, 1675 (broad, intense), 1590, 1470, 1180, 900, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.70–8.30 ppm (complex m, aromatic); no NH absorption.

N-Benzoyl-2-aminotolane

A turbid solution of 10.0 g (31.0 mmoles) of N-(2-iodophenyl) benzamide and 3.35 g (32.8 mmoles) of phenylacetylene in 300 ml of a 2:1 toluene-triethylamine solvent mixture was deaerated and heated to 60°C under argon. The catalyst was introduced in the order of 300 mg of triphenylphosphine, 100 mg of palladium[II] chloride and 200 mg of copper[I] iodide. The resulting mixture was heated to 80–90°C. Precipitation commenced in 10 min. After 3 hr at 80–90°C, the mixture was cooled and filtered to remove 7.10 g (31.0 mmoles, 100%) of triethylamine hydroiodide. The yellow filtrate was concentrated to a solid which was recrystallized from 400 ml of absolute ethanol: yield, 8.90 g (30.0 mmoles, 96.7%); mp 114–115°C; IR (KBr) 3320 (intense), 1660 (intense), 1585, 1530 (intense), 1495, 1450, 1330, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.85–7.70 (m, 11H, $C_6H_4C\equiv C$-Ph and meta-protons on PhC=O), 7.80–8.15 (m, 2H, ortho-protons on PhC=O), 8.60 (m, 1H, para-proton on PhC=O), and 8.88 ppm (bs,1H, NH).

2,2'-Bis(phenylethynyl)benzalazine

A solution of 20.6 g (100 mmoles) of 2-(phenylethynyl)benzaldehyde in 200 ml of absolute ethanol was treated with 2.50 g (50.0 mmoles) of 100% hydrazine hydrate. After 10 min at 25°C, a pale yellow precipitate began to accumulate. After 30 min, the precipitate appeared copious and the mixture was diluted with 100 ml of ethanol to facilitate stirring. The reaction

was stopped after a total period of 1.5 hr and the product was isolated, washed with methanol and dried to yield 16.4 g (40.2 mmoles, 80.4%): mp 155–157°C; IR (KBr) 1620, 1490, 755 cm $^{-1}$.

2-(Phenylethynyl)benzaldehyde Phenylhydrazone

A solution of 6.00 g (29.1 mmoles) of 2-(phenylethynyl)benzaldehyde in 150 ml of absolute ethanol was treated with 3.15 g (29.1 mmoles) of phenylhydrazine in 50 ml of ethanol. The reaction was slightly exothermic. After 30 min at 25°C, the solution was treated with 3 drops of 85% phosphoric acid and heated at reflux for 2 hrs. Upon cooling, a massive precipitate was obtained and was recrystallized once from hexane to yield 7.40 g (25.0 mmoles, 85.9%) of off-white crystals: IR (KBr) 2200 (very weak), 1605, 1580, 1520, 1495, 1265, 1155, 755 cm^{-1}

Benzalazine and 1,4-Dichloro-1,4-diphenyl-2,3-diazabutadiene

A mixture of 42.4 g (400 mmoles) of benzaldehyde and 10.0 g of 100% hydrazine hydrate in 400 ml of absolute ethanol was stirred for 30 min. The slightly exothermic reaction mixture was cooled and the bright yellow crystals were collected and dried at 50°C/0.1 torr, yielding 31.7 g (152 mmoles, 76.2%); mp 91–92°C, literature (References 132, 133) value was 92–92.5°C; IR (KBr) 1625 (intense), 1575, 1490, 1450, 1305, 1290, 1210, 960, 750, 690 cm^{-1}.

A solution of 11.4 g (54.8 mmoles) of benzalazine in 300 ml of carbon tetrachloride was gently stirred while a continuous flow of chlorine gas was passed through over a period of 18 hr. The solution was concentrated and the residue was taken up in hexane and cooled to −78°C to yield 3.95 g (14.2 mmoles, 26.0%) of white crystals: mp 117–118°C; IR (KBr) 1600, 1575, 1490, 1450, 1225, 925, 765, 685 cm^{-1}; MS (70 eV) m/e 276, 278 (molecular ions), 241, 138.

1,2-Dibenzoylhydrazine and 2,5-Diphenyl-1,3,4-oxadiazole

To a solution of 56.0 g (399 mmoles) of benzoyl chloride in 150 ml of anhydrous pyridine at 0°C was added dropwise 10.0 g (200 mmoles) of hydrazine hydrate (100% assay). Immediately a white precipitate was formed. After the addition, the mixture was stirred at 25°C for 2 hr and then diluted with 1 liter of water. The white solid was isolated by filtration, washed with 50% aqueous ethanol and air dried: yield, 44.2 g (184 mmoles, 92.1%); mp 236–238°C; IR (KBr) 3200 (broad, intense), 1700, 1665, 1630 (intense), 1580, 1540, 1490, 1290 (intense), 690 cm^{-1}.

A mixture of 44.1 g (184 mmoles) of 1,2-dibenzoylhydrazine and 35 ml (58.5 g, 491 mmoles) of thionyl chloride in 400 ml of anhydrous benzene was heated at reflux for 2 hr.

After most of the volatile material was evaporated, the residue was mixed with 200 ml of hexane to precipitate an off-white solid which was subsequently recrystallized from 200 ml of absolute ethanol to afford light weight crystals of 2,5-diphenyl-1,3,4-oxadiazole: yield, 27.5 g (124 mmoles, 67.3%); mp 137–138°C; MS (70 eV) m/e 224 (molecular ion + 2H), 168 (base peak), 106, 77; ^{1}H NMR ($CDCl_3$) δ 7.31–7.71 (m, 6H, aromatic H_3, H_4, H_5) and 7.92–8.32 ppm (m, 4H, aromatic H_2, H_6).

1,2-Bis(2-bromobenzoyl)hydrazine and 1,2-Bis(2-bromobenzoyl)diazine

To a solution of 43.9 g (200 mmoles) of 2-bromobenzoyl chloride in 100 ml of anhydrous pyridine at 0°C was added dropwise 5.0 g (100 mmoles) of hydrazine hydrate (100% assay). The mixture was stirred for an additional 2 hr at 25°C, diluted with 1 liter of water, and filtered to give a white solid which was dried to a constant weight at 70°C/0.1 torr (16 hr): yield, 27.0 g (67.8 mmoles, 67.8%); ^{1}H NMR (DMSO-d_6) δ 6.68 (m, 4H, aromatic) and 9.68 ppm (s, 1H, NH).

A mixture of 5.00 g (12.6 mmoles) of the above product in 200 ml of dichloromethane and 200 ml of water was stirred while chlorine gas was bubbled through. Slowly the solid entered into solution and the organic phase turned red-orange. After 1 hr, thin-layer chromatography indicated total absence of the starting material. A single spot (TLC, silica gel, 1:1 dichloromethane-hexane) corresponding to the product was observed. The organic phase was separated, washed with 200 ml of 10% aqueous sodium bicarbonate solution and dried over anhydrous magnesium sulfate. After solvent removal, the oily residue was taken up in 100 ml of ether and mixed with 100 ml of hexane. Slow evaporation down to dryness caused the formation of a pale yellow crystalline solid which was isolated by filtration and washed with cold hexane: yield, 3.60 g (9.09 mmoles, 72%); IR (KBr) 1720 (broad, intense), 1590, 1470, 1430, 1280–1240 (very broad, intense), 1140, 1090, 1030, 740 cm^{-1}.

2-Iodobenzoyl Chloride and 1,2-Bis(2-iodobenzoyl)hydrazine

A slurry of 52.0 g (21.0 mmoles) of 2-iodobenzoic acid in 50 ml dichloromethane was mixed with 50 ml of thionyl chloride and the mixture was heated at reflux for 16 hr. A stream of nitrogen was passed through the hot solution to evaporate dichloromethane and other volatiles. The viscous oil solidified on cooling to 25°C under nitrogen. The solid was dissolved in 100 ml of lukewarm anhydrous hexane and the solution cooled to yield while fluffy crystals: yield, 36.3 g (13.6 mmoles, 64.9%); mp 40–41°C; IR (CH_2Cl_2 solution) 1785 (intense), 1585, 1435, 1195, and 860 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.24 (t x d, 1H, J = 7.2, 1.8 Hz, aromatic H_4), 7.52 (t x d, 1H, J = 7.2, 1.8 Hz, aromatic H_5), and 8.10 ppm (d x m, 2H, aromatic H_3 and H_6).

To solution of 19.7 g (74.0 mmoles) of 2-iodobenzoyl chloride and 25 ml of anhydrous pyridine in 100 ml of anhydrous dichloromethane was added dropwise 1.02 g (38.4 mmoles) of hydrazine hydrate (100% assay) a vigorous reaction ensued. The mixture was stirred for an additional hr at 25°C. The white precipitate which formed was filtered off. The two phase filtrate was warmed to evaporate dichloromethane. The solid dispersion was isolated by filtration. The combined crops of solids was washed with 1:1 hexane-ether and dried to a constant weight at 70°C/0.1 torr (8 hr): yield, 12.7 g (25.9 mmoles, 69.9%); mp 278–279°C; IR (KBr) 3210, 1600, 1490, 1455 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.00–7.70 (m, 6H, aromatic H_3, H_4, H_5), 7.90, 8.05 (broad d, 2H, aromatic H6) and 10.50 ppm (s, 2H, NH).

Anal. for $C_{14}H_{10}I_2O_2N_2$(492.06):

Calculated: C, 34.17; H, 2.05; I, 51.58; N, 5.69.
Found: C, 34.09; H, 1.82; I, 51.72; N, 5.77.

2-(Phenylethynyl)benzoic Acid and 2-(Phenylethynyl)benzoyl Chloride

An emulsion of 8.00 g (38.8 mmoles) of 2-(phenylethynyl)benzaldehyde in 200 ml of water was warmed to 100°C and treated with 6.5 g of potassium permanganate in 200 ml of water. The mixture was heated at 100°C for 2 hr and treated with 10 g of sodium bisulfite in 20 ml of acidified water. The brown manganese dioxide precipitate dissolved to yield soluble manganese sulfate. The oily droplets were extracted with 2 × 50 ml of dichloromethane. The solvent was removed and the residual red oil yielded 7.00 g (31.5 mmoles, 81.2%) of crystals upon standing. The identity of the acid product was ascertained by IR and ^1H NMR. The NMR spectrum ($CDCl_3$) δ 6.70–8.30 (m, 9H, aromatic) and 10.70 ppm (s, 1H, $CO_2\underline{H}$) showed that the proton absorption was identical to that of the aldehydic proton of 2-(phenylethynyl)-benzaldehyde but the aromatic region showed dissimilarities between the two compounds.

The carboxylic acid was mixed with 10 g of thionyl chloride, heated at reflux for 2 hr, and cooled with a stream of argon. After the volatiles were removed, the residual oil was purified by distillation at 158–163°C/0.3 torr to give an orange-yellow oil: yield, 5.20 g (21.6 mmoles, 68.6%); IR (neat) 2210 (medium, sharp), 1770, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) 6.60–8.30 ppm (m, aromatic) and no absorption from 8–12 ppm.

2-(2-Bromophenyl)benzimidazole

To a solution of 14.6 g (13.5 mmoles) of ortho-phenylenediamine in 200 ml of ethanol was added a mixture of 25.0 g (13.5 mmoles) of 2-bromobenzaldehyde and 60 g of sodium bisulfite

in 500 ml of 50% aqueous ethanol. The resulting mixture was heated at reflux for 4 hr. On cooling, white crystals appeared. They were filtered off and dried under vacuum at 100°C/0.1 torr to constant weight: yield, 28.2 g (10.3 mmoles, 76.5%); mp 237.5°–238.5°C; ^{1}H NMR (DMSO-d_6) δ 7.00–7.10, 7.12–7.80 (three sets of m's, aromatic) and 11.0 ppm (broad absorption, 1H, NH).

Phenylethynylation of 2-(2-Bromophenyl)benzimidazole. Incomplete Conversion to 11-Benzylidene-1H-isoindolo[2,1a]benzimidazole

To a deaerated mixture of 200 ml of 3:1 triethylamine-N,N-dimethylacetamide containing 100 mg of triphenylphosphine, 80 mg of dichlorobis(triphenylphosphine)palladium [II], and 40 mg of anhydrous copper[I] iodide, was added 2.50 g (9.16 mmoles) of 2-(2-bromophenyl)-benzimidazole and then 1.00 g (9.80 mmoles) of phenylacetylene. The mixture was heated under argon at 90°C for 36 hr. After cooling, the mixture was diluted with twice the volume of ether and filtered to remove ca. a 30% yield of triethylamine hydrobromide. The filtrate was redissolved in 100 ml of ether and the solution was washed eight times with 100 ml of water and once with saturated ammonium chloride solution. After drying the organic phase over anhydrous magnesium sulfate and concentrating, the resulting crude product was examined by NMR spectrometry, which showed the presence of 67% of starting material and 33% of a new compound. This compound was isolated by silica gel column chromatography, eluting with dichloromethane, and identified as 11-benzylidene-1H-isoindolo[2,1a]benzimidazole based on its IR, MS, ^{13}C and 250 MHz ^{1}H NMR spectral characteristics.

11-Benzylidene-1H-isoindolo[2,1a]benzimidazole

A mixture of 8.80 g (4.27 mmoles) of 2-(phenylethynyl)benzaldehyde and 4.70 g (4.35 mmoles) of ortho-phenylenediamine in 400 ml of 50% aqueous ethanol containing 25 g of sodium bisulfite was heated at reflux for 5 hr. On cooling, crystals appeared and were filtered and washed thoroughly with 50% aqueous ethanol. The mp was 177–179°C. After drying at 100°C/0.1 torr to constant weight, the mp was raised to 181–182°C. GC–MS analysis indicated the presence of only one product. Yield, 8.50 g (2.89 mmoles, 67.7%); IR (KBr) 3180, 3140, 1645, 1530, 1500, 1455, 1330, 1320, 1280, 1240, 1160 and 740 cm^{-1}; MS (70eV) m/e 294 (molecular ion, base peak), no significant fragments; 250–MHz ^{1}H NMR ($CDCl_3$) δ 6.49, 6.52 (d x t, 1H, J's = 8.3, 1.0 Hz, aromatic H_8), 6.92 (bs, 1H, vinyl), 7.02 (d x d x d, 1H, J's = 8.3, 7.5, 1.0 Hz, aromatic H_7), 7.41 (d x d x d, 1H, J's = 8.3, 7.5, 1.0 Hz, aromatic H_6), 7.62 (m, 5H, H's on pendent phenyl), 7.68–7.74 (m, 3H, aromatic H_2, H_3, H_4), 7.99, 8.02 (d x t, 1H, J's = 8.3, 1.0 Hz, aromatic H_5), and 8.89–8.92 ppm (m, 1H, aromatic H_1); ^{13}C NMR ($CDCl_3$) δ 148.45, 144.54,

137.68, 134.88, 131.74, 130.90, 130.17, 129.99, 129.55(2), 129.10(2), 127.96, 126.76, 125.28, 124.29, 123.17, 121.36, 119.92, 114.22, 112.67 ppm.

Anal. for $C_{21}H_{14}N_2$ (294.36):

Calculated: C, 85.69; H, 4.79; N, 9.52.
Found: C, 85.52; H, 4.81; N, 9.40.
C, 85.39; H, 5.03; N, 9.73.

cis- and trans-1,2-Dibromobenzocyclobutenes

A slurry of 50.0 g (118 mmoles) of $\alpha,\alpha,\alpha',\alpha'$-tetrabromo-o-xylene and 75.0 g (500 mmoles) of sodium iodide in 250 ml of absolute ethanol was heated to reflux over 30 min. The intense iodine color began to appear. After heating at reflux for 44 hr, the mixture was cooled and poured into 1.2 liters of water containing 30 g of sodium bisulfite. The organic droplets were extracted with 2 × 300 ml of hexane. The organic extracts were combined, washed once with 500 ml of water and dried over anhydrous magnesium sulfate. After solvent removal, the oily residue was eluted through a silica gel column with 600 ml of hexane. The eluate was concentrated to 100 ml and a white crystalline solid was obtained. The slurry was cooled briefly at −78°C and filtered to obtain 24.5 g (93.5 mmoles, 79.2%) of the product: IR (KBr) 1465, 1450, 1345, 1324, 1202, 1175, 1168, 1150, 1126, 875, 757, 660, 654, 647 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.40, 5.52 (2 distorted s, methine protons of the cis and trans products) and 7.00–7.55 ppm (complex m, 4H, aromatic).

Continuous elution of the column with 1.2 liters of hexane yielded long needles (1.5 g), mp 130–131°C; ^1H NMR ($CDCl_3$) δ 5.95 (s, 1H), 5.60, 6.10 (AB quartet, 2H, J = 4 Hz, vinylic), and 6.90–7.45 ppm (complex m, 4H, aromatic).

Benzocyclobutene and 1-Bromobenzocyclobutene

The literature procedure (Reference 154) was used with minor modifications. To a solution of 27.5 g (105 mmoles) of 1,2-dibromobenzocyclobutene and 20 g (61.4 mmoles) of tri-n-butyltin chloride in 200 ml anhydrous tetrahydrofuran (THF) was added 2.8 g (74.1 mmoles) of lithium aluminum hydride in small portions so that a moderate reflux condition was maintained. After the addition, the slurry was stirred at reflux for 4 hr, cooled to ambient temperature and transferred to a 600-ml beaker before being treated by dropwise addition with 5 ml of water, 5 ml of 10% aqueous sodium hydroxide and 5 ml of water again. The granular solid residue was filtered and washed with 50 ml of ether.

The filtrate was vacuum-transferred at 0.2 torr to a receiver cooled in liquid nitrogen. The undistillable residual oil was unreacted tri-n-butyltin chloride and impurities. The distillate was shaken with 1 liter of water, washed with 200 ml of saturated sodium chloride solution and dried over magnesium sulfate. Distillation through a 15-cm Vigreux column removed the volatiles and the residual oil was distilled via a short path apparatus. The fraction that boiled at 140–145°C was collected. The purity was ascertained by NMR. The lower boiling earlier cuts were combined and redistilled at 24°C/0.25 torr to yield more pure product. The combined yield was 3.80 g (36.5 mmoles, 34.8%); ^{1}H NMR ($CDCl_3$) δ 3.16 (s, 4H, $C\underline{H}_2$) and 7.10 ppm (symmetrical m, 4H, aromatic).

The benzocyclobutene product obtained was mixed with 7.00 g (39.3 mmoles) of N-bromosuccinimide in 50 ml carbon tetrachloride and 0.1 g of benzoyl peroxide. The mixture was heated at reflux for 3.5 hr, cooled, and the succinimide by-product filtered off. The filtrate was concentrated, washed through a column of silica gel with hexane and concentrated to a pale yellow oil. Distillation at 35–39°C/0.1 torr yielded 4.10 g (22.4 mmoles, 61.4%) of 1-bromobenzocyclobutene: IR (neat) 2930, 1457, 1205, 1178, 1162, 871, 748 cm^{-1}; MS (70 eV) m/e 182, 184 (molecular ions), 103 (base peak); ^{1}H NMR ($CDCl_3$) δ 3.26, 3.51 (d x d, 1H, J_{gem} = 15 Hz, J_{cis} = 2 Hz), 3.72, 4.00 (d x d, 1H, J_{gem} = 15 Hz, J_{trans} = 5 Hz), 5.40 (d×d, J's = 2 Hz, 5 Hz) and 7.26 ppm (m, 4H, aromatic).

Benzocyclobutenol via 1-Acetoxybenzocyclobutene

A solution of 49.0 g (357 mmoles) of anthranilic acid in 150 ml of warm vinyl acetate and 57 ml (49.7 g, 424 mmoles) of iso-amyl nitrite were added concurrently over 1 hr to 1 liter of refluxing vinyl acetate. Gas evolution was brisk. The mixture was heated at reflux for 1 more hr and 1 liter of vinyl acetate was distilled. The remaining volatiles were removed on a rotary evaporator and the residue was dissolved in 400 ml of dichloromethane, washed three times with 100-ml portions of water, dried over anhydrous magnesium sulfate, concentrated and distilled at 59–62°C/0.35 torr to yield 25.2 g (155 mmoles, 43.5%) of 1-acetoxybenzocyclobutene; IR (film) 3080, 2970, 1730 (intense), 1235, 1040, 745 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.00 (s, 3H, $C\underline{H}_3$), 3.12 (d x d, 1H, J's = 14 Hz, 2 Hz, $C\underline{H}_{cis}$ H_{trans}), 3.60 (d x d, 1H, J's = 14 Hz, 5 Hz, $C\underline{H}_{cis}$ H_{trans}), 5.80 (d x d, 1H, J's = 5 Hz, 2 Hz, methine H) and 7.18 ppm (bs, 4H, aromatic).

A solution of 25.0 g (154 mmoles) of 1-acetoxybenzocyclobutene in 150 ml of methanol was stirred while an aqueous solution of 40 g of sodium carbonate decahydrate was introduced. The resulting cloudy light yellow mixture was stirred at 25°C for 20 hrs and worked up by extraction with 3 × 300 ml of ether. The combined ethereal extracts were washed with 3 × 500 ml of water, dried over anhydrous magnesium sulfate and concentrated to yield 15.0 g (125 mmoles, 81.2%) of benzocyclobutenol; mp 58–60°C; IR (KBr) 3300, 3200 (broad,

intense), 1455, 1210, 1110, 1055 (intense), 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.12 (bd, 1H, J's = 14 Hz, 0.5 Hz, $CH_{cis}H_{trans}$), 3.70 (d x d, 1H, J's = 14 Hz, 4 Hz, $CH_{cis}H_{trans}$), 5.38 (bs, 2H, methine H and OH) and 7.42 ppm (distorted s, 4H, aromatic).

Benzocyclobutenol via 2-Bromostyrene oxide

To a solution of 37.8 g (300 mmoles) of dimethyl sulfate in 140 ml of acetonitrile was added dropwise at 25°C a solution of 20.5 g (330 mmoles) of dimethyl sulfide in 60 ml of acetonitrile. The colorless solution was stirred at 25°C for 17 hr and then treated in succession with 17.8 g (330 mmoles) of sodium methoxide and 37.0 g (200 mmoles) of 2-bromobenzaldehyde. The final mixture was stirred for 2 hr. Dimethylsulfide and acetonitrile were distilled off at 80°C. The concentrate was treated with 100 ml of water to allow two phases to separate. The organic phase was isolated, washed with 100 ml of water and dried over anhydrous magnesium sulfate. Distillation at 57–58.5°C/0.025 torr gave a colorless liquid, 32.2 g (162 mmoles, 81.0%); ^1H NMR ($CDCl_3$) δ 2.61 (d x d, 1H, J's = 6 Hz, 2 Hz), 3.18 (d x d, 1H, J's = 6 Hz, 4 Hz), 4.16 (d x d, 1H, J's = 4 Hz, 2 Hz), 7.00–7.72 ppm (m, 4H, aromatic).

A higher boiling distillate was obtained which upon standing yielded white crystals (mp 78–79°C), identified as 2-bromobenzyl alcohol; ^1H NMR ($CDCl_3$) δ 4.22 (t, 1H, OH, disappears with D_2O treatment), 4.70 (d, 2H, benzylic), 6.94–7.70 ppm (m, 4H, aromatic).

To a deaerated solution of 10.0 g (50.3 mmoles) of 2-bromostyrene oxide in 50 ml of anhydrous THF at −78°C was added 400 ml of a 0.2M solution of magnesium bromide in ether-toluene and 31.2 ml of a 1.6M solution of n-butyllithium in hexane. The mixture was stirred at −78°C for 1 hr and allowed to warm to 25°C over 2 hr. After treatment with 200 ml of saturated ammonium chloride solution and separating the phases, the organic phase was washed with 2 x 200 ml of water, dried over anhydrous magnesium sulfate and concentrated to a viscous oil which was purified by silica gel column chromatography: yield, 3.38 g (28.2 mmoles, 56.0%): mp 58–60°C. The IR and NMR spectra were identical to those of an authentic sample of benzocyclobutenol.

Benzocyclobutenone

A standard chromic acid reagent solution was prepared by dissolving 100 g of sodium dichromate dihydrate in 300 ml of water, followed by addition of 136 g of 98% sulfuric acid. The solution was then diluted to 500 ml.

A solution of 30.0 g (250 mmoles) of benzocyclobutenol in 100 ml of ether was cooled to 0°C and treated by dropwise addition of 120 ml with chilled chromic acid reagent over 5 min. A second portion of the reagent was then added. Vigorous stirring was maintained for another 5 min. The upper layer was separated and the lower layer was extracted with 3 × 100 ml of ether. The combined ethereal extracts were washed with 3 × 200 ml of water, dried

over anhydrous magnesium sulfate, concentrated and distilled at 65–68°C/1.5 torr to give 17.0 g (144 mmoles, 57.6%) of benzocyclobutenone; IR (film) 1773, 1754 (intense), 1577, 1460, 1273, 1136, 957, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.90 (s, 2H, $C\underline{H}_2$) and 7.10–7.60 ppm (m, 4H, aromatic).

Continuous distillation at 0.1 torr yielded a higher boiling fraction which solidified upon standing. The solid, identified as phthalide, was recrystallized from hexane: yield, 7.10 g (51.4 mmoles, 20.6%), mp 67–69°C; IR (KBr) 1765 (broad, intense), 1480, 1450, 1380, 1330, 1300, 1230, 1065, 1015, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.32 (s, 2H, $C\underline{H}_2$) and 7.32–8.10 ppm (m, 4H, aromatic).

1-Bromobenzocyclobutene via Benzocyclobutenol

To 73.4 g of phosphorus pentabromide in 300 ml of carbon tetrachloride at 0°C was added dropwise a solution of 20.0 g (166 mmoles) of benzocyclobutenol in 300 ml of carbon tetrachloride over 30 min. The reaction mixture was allowed to warm to 25°C over 2 hrs and was poured into 1 liter of ice-water. The organic layer was washed with 500 ml each of saturated sodium bicarbonate solution, 20% aqueous sodium bisulfite solution, and water. After drying and concentrating, the residual oil was distilled at 49–53°C/0.25 torr to yield 29.5 g (161 mmoles, 97.1%) of 1-bromobenzocyclobutene. The IR and NMR spectral characteristics matched with those of an authentic sample.

(3-Phenyl-2-propynylidene)benzocyclobutene

(3-Phenyl-1,2-propadienyl)triphenylphosphonium bromide was prepared by the reaction of 3-phenylpropargyl bromide and triphenylphosphine in benzene (92% yield, mp 212°C with decomposition). To a deaerated anhydrous solution of 4.90 g (11.0 mmoles) of the phosphonium salt in 50 ml of tetrahydrofuran at −78°C was added dropwise 16 ml of a 1.6M solution of n-butyllithium in hexane. After 30 min, the ylide solution was treated with 1.18 g (10.0 mmoles) of benzocyclobutenone and was allowed to warm to 25°C over 2 hrs.

The mixture was diluted with an equal volume of ether and filtered to remove most of the triphenylphosphine oxide formed. The filtrate was washed with 200 ml of 1 N aqueous hydrochloric acid and 200 ml of water. After drying and solvent removal, the residual oil was filtered through a short column of silica gel with hexane eluant. The eluate was concentrated to yield white crystals: yield, 830 mg (3.84 mmoles, 38.4%); mp 74–75°C; IR (film) 2040 (weak), 1590, 1495, 1440 (intense), 1190, 1170, 750, 720, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.72 (distorted d, 2H, J = 1 Hz, $C\underline{H}_2$), 5.86 (t, 1H, J = 1 Hz, vinyl H), 7.14 (s, 5H, C≡C$\underline{Ph}$) and 7.00–7.60 ppm (m,4H, aromatic).

(2-Bromobenzylidene)benzocyclobutene

(2-Bromobenzyl)triphenylphosphonium bromide was prepared by heating a mixture of 25.0 g (100 mmoles) of 2-bromobenzyl bromide and 26.2 g (100 mmoles) of triphenylphosphine in 300 ml of anhydrous toluene at 100°C for 18 hr. The phosphonium salt was filtered off, washed with ether and dried to a constant weight of 50.8 g (99.2 mmoles, 99.2%); ^{1}H NMR ($CDCl_3$) δ 5.46 (d, 2H, J = 14 Hz, CH_2P), and 7.00–8.10 ppm (m, 19H, aromatic).

Anal. for $C_{25}H_{21}Br_2P$ (512.24):

Calculated: C, 58.61; H, 4.13; Br, 31.20; P, 6.05.
Found: C, 58.54; H, 4.19; Br, 30.97; P, 5.90.

A slurry of 21.49 g (41.96 mmoles) of the phosphonium salt in 200 ml of deaerated anhydrous tetrahydrofuran (THF) was cooled to −78°C and treated with 29 ml of a 1.6 M hexane solution of n-butyllithium. The ylide obtained was dark red. The mixture was warmed to 25°C over 30 min, cooled again to −78°C and treated with 4.614 g (39.10 mmoles) of benzocyclobutenone. The mixture was warmed to 25°C over 1 hr and stirred at 25°C for 18 hr. The solids were filtered off and the filtrate was diluted with 500 ml of 10% aqueous hydrochloric acid and extracted with 3 × 200 ml of ether. The organic extracts were combined, dried and concentrated to an oil. Silica gel column chromatography, eluting with hexane, yielded a solid which was recrystallized from cold hexane to give 1.187 g (4.380 mmoles, 11.2%) of probably the E-isomer: mp 79–80°C; IR (KBr) 3090, 1675 (intense), 1600, 1480 (intense), 1445, 1350, 1185, 1030 (intense), 875, 750 (broad intense); ^{1}H NMR ($CDCl_3$) δ 3.80 (distorted s, 2H, CH_2) and 6.78–7.60 ppm (m, 9H, aromatic and vinylic).

Anal. for $C_{15}H_{11}Br$ (271.16):

Calculated: C, 66.44; H, 4.09; Br, 29.47.
Found: C, 66.46; H, 4.77; Br, 29.25.

Subsequent elution of the column with 2 : 3 dichloromethane-hexane yielded 0.872 g of a mixture of the E,Z-isomers. The total yield of the E,Z-isomer mixture was 19.4%.

(2-Phenylethynylbenzylidene)benzocyclobutene. From 1-Bromobenzocyclobutene.

(Benzocyclobutenyl)triphenylphosphonium bromide was prepared by melting 6.014 g (22.95 mmoles) of triphenylphosphine inside a flame dried, argon-purged reaction flask and then treating the melt with 1.929 g (10.54 mmoles) of 1-bromobenzocyclobutene. Immediately

an orange yellow precipitate was formed. The mixture was heated at 140°C under argon for 16 hrs, cooled to 25°C, mixed with 100 ml of ether, stirred for 5 min and then filtered to afford 3.602 g (8.09 mmoles, 76.8%) of tan-colored powdery product.

To a suspension of 3.536 g (7.946 mmoles) of the phosphonium bromide in 100 ml of anhydrous tetrahydrofuran under argon at −78°C was added 5.5 ml of a 1.6 M solution of n-butyllithium in hexane. The bright orange solution was stirred and warmed to 25°C over 30 min, cooled back down to −78°C and treated with a solution of 1.555 g (7.549 mmoles) of 2-(phenylethynyl)benzaldehyde in 20 ml of anhydrous tetrahydrofuran. The mixture was warmed to 25°C over 1 hr, stirred at 25°C for 16 hr, diluted with an equal volume of ether and filtered. The filtrate was concentrated to a syrupy residue, redissolved in ether, extracted with 2 × 100 ml of water, dried over magnesium sulfate and concentrated. Silica gel column chromatography eluting with 1 : 3 dichloromethane-hexane eventually yielded 1.00 g (3.42 mmoles, 43.1%) of product: IR (KBr) 2040, 1590, 1495, 1170, 750 cm^{-1}; MS (70 eV) m/e 292 (molecular ion); ^1H NMR ($CDCl_3$) δ 3.76, 3.92 (two s, 2H, $C\underline{H}_2$), 6.82 (bs, 1H, vinylic H) and 7.00–8.10 ppm (m, 13H, aromatic).

Benzocyclobutene-1-carboxylic Acid, Benzocyclobutene-1-carbonyl chloride and N-(2-Benzocyclobutene-1-carboxamide

The magnesium turnings (0.796 g, 32.73 mmoles) were covered with 10 ml of anhydrous tetrahydrofuran (THF) under argon and treated with dropwise addition of a solution of 4.955 g (27.08 mmoles) of 1-bromobenzocyclobutene in 40 ml of anhydrous THF. The supernatant liquid turned brown and the reaction flask was warmed to touch. After the addition, the reaction mixture was heated at reflux for 10 min, cooled and treated with 5 g of pulverized Dry Ice. After the system returned to 25°C, the mixture was mixed with 100 ml of 10% aqueous hydrochloric acid and extracted with 3 × 75 ml of ether. The combined ethereal fractions were dried over magnesium sulfate and concentrated to an oil. The crude yield was 2.679 g (18.10 mmoles, 66.84%). The NMR spectrum was consistent with the structure of the acid: ^1H NMR ($CDCl_3$) δ 3.44 (d, 2H, J = 4 Hz, $C\underline{H}_2$), 4.26 (t, 1H, J = 4 Hz, C<u>H</u>), 7.20 (distorted s, 4H, aromatic), and 11.92 ppm (s, 1H, $CO_2\underline{H}$).

The crude acid was used without purification. It was mixed under argon with 2 ml of freshly distilled thionyl chloride and heated at reflux for 30 min. The volatiles were evaporated to leave 2.940 g (17.70 mmoles, 97.6%) of a mobile liquid; IR (neat) carbonyl at 1800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.50 (d, 2H, J = 4 Hz, $C\underline{H}_2$), 4.62 (t, 1H, J = 4 Hz, C<u>H</u>) and 7.24 ppm (m, 4H, aromatic).

The acid chloride was added to a vigorously stirred mixture of 3.368 g (17.45 mmoles) of 2-aminotolane, 20 ml of benzene and 100 ml of water at 80–90°C. After 0.5 hr, the mixture was treated with 50 ml of 10% sodium hydroxide solution. The organic fraction after drying

yielded a white powdery solid, 4.52 g (14.0 mmoles, 80.2%); mp 115°C; IR (KBr) 3380, 3300, 1695 (intense), 1665 (intense), 1580 (intense), 1520 (intense, broad), 1445, 1305, 1180, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.56 (distorted d×d, 2H, CH_2), 4.44 (distorted d×d, 1H, methine), 6.70–7.50 (m, 8H, aromatic), 7.40 (s, 5H, C≡C-Ph) and 8.40 ppm (broad absorption, 1H, NH).

Attempted Oxidative Addition of Bromobenzocyclobutene with Tetrakis-(triphenylphosphine)palladium[0]

Tetrakis(triphenylphosphine)palladium[0] was synthesized by a standard procedure (Reference 119). The bright yellow complex was air sensitive and was kept under argon in a Dry Box until used.

A yellow orange solution of 10.0 g (8.67 mmoles) of the palladium[0] complex in 75 ml of carbon monoxide–saturated benzene was treated with dropwise addition of a solution of 2.50 g (13.7 mmoles) of 1-bromobenzocyclobutene in 25 ml deaerated benzene under carbon monoxide at 25°C. The mixture was stirred at 25°C for 16 hr and then diluted with an equal volume of ether. The yellow solid was removed by filtration under argon. IR of the solid showed no metal-carbonyl absorption characteristic of an acylpalladium[II] complex. The solid also appeared to be sensitive to air as evident by the rapid darkening of color upon standing.

The filtrate was concentrated to a solid residue. After washing with hexane, the white solid weighed 4.57 g. IR showed that it was triphenylphosphine, mp 78°C. This corresponded to a quantitative recovery of the two dissociated phosphine ligands. On this basis, the yellow palladium complex obtained probably was $Pd(PPh_3)_2$.

The hexane washing yielded an oil after solvent removal. Its identity as 1-bromobenzocyclobutene was ascertained by NMR spectrometry.

Thermal Intramolecular Cyclization Reaction of N-(2-Phenylethynyl)phenyl Benzocyclobutene-1- carboxamide

N-(2-Phenylethynyl)phenyl benzocyclobutene-1-carboxamide (518 mg)) was heated under argon at 225 ± 5°C for 2 hr, cooled to 25°C and triturated with ether. The solution yielded no precipitate and was concentrated. The residual oil was mixed with carbon tetrachloride and a pale yellow microcrystalline solid was obtained. Thin-layer chromatography indicated complete absence of the starting material. Column chromatography through silica gel yielded a white microcrystalline solid in the dichloromethane eluate. The white solid remained white up to 240°C and gradually turned yellow. Near 300°C, it turned brown but did not melt even at 315°C; IR (KBr) 3450 (broad), 1650 (broad, intense), 1100 (broad), 755 cm^{-1}; MS (70 eV) m/e

at 323 (molecular ion), 246, 228, 217; ^{1}H NMR ($CDCl_3$) δ 3.14–3.45 (distorted doublets, 2H, CH_2), 4.69 (distorted d, 1H, methine), 7.06 (s, 5H, pendant Ph), 6.45–7.80 (complex m, ca. 8H, aromatic) and 9.00 ppm (distorted d, 1H, NH).

Anal. for $C_{23}H_{17}NO$ (323.40):

Calculated: C, 85.42; H, 6.20; N, 5.07.
Found: C, 85.90; H, 6.63; N, 4.15.

1,2-Bis(1-hydroxy-3-phenyl-2-propynyl)benzene and Subsequent Oxidation

Into a flame dried, argon purged reaction flask were placed 36.2 g (1.49 moles) of magnesium turnings and 200 ml of anhydrous tetrahydrofuran (THF). A 100-ml solution of 158 g of ethyl bromide in THF was added dropwise so that a controlled vigorous reflux was maintained. After the addition, the mixture was allowed to reflux for 30 more min before introducing a solution of 146 g (1.43 moles) of phenylacetylene in 150 ml of THF. The mixture was then heated at reflux for 1 more hr and allowed to react with 25.0 g (187 mmoles) of phthalic dialdehyde, added dropwise as a 150 ml THF solution. The final mixture was again heated at reflux for 1 hr, cooled, diluted with 500 ml of ether, and then hydrolyzed with 250 ml of saturated ammomium chloride solution. The organic phase was separated, washed with 250 ml each of 1N hydrochloric acid, water, saturated sodium bicarbonate and then water again. After drying and removal of solvent, an oily residue was obtained. IR showed the expected OH absorptions, a weak sharp band at 2220 cm^{-1} and no aldehyde absorptions which could indicate starting material.

The oil was used without purification. To a solution of 51.0 g of the crude oil obtained above in 300 ml of ether at 0°C was added 300 ml of a 0.67 M aqueous chromic acid solution. The mixture was vigorously stirred for 20 min before work-up. The ethereal phase was washed with water, with 4 × 300 ml of saturated sodium bicarbonate solution and then with 4 × 300 ml of water again. After drying and solvent removal, an orange-yellow powdery solid was obtained and was recrystallized two times from benzene-ethanol: mp 283°C; IR (KBr) 1670 (intense), 1620, 1600, 1585, 1500, 1415, 1390, 1340, 1275 (intense), 985 cm^{-1}.

1-(2-Phenylethynyl)phenyl-3-phenylpropynol and 1-(2-Phenylethynyl)phenyl-3-phenylpropynone

Magnesium turnings (1.973 g, 81.13 mmoles) were covered with 10 ml of anhydrous tetrahydrofuran (THF) and treated with dropwise addition of 8.785 g (80.60 mmoles) of ethyl

bromide in 35 ml of THF. The reaction rapidly started and a vigorous reflux was maintained throughout the addition. After 30 min, the mixture was cooled and treated with 8.192 g (80.31 mmoles) of phenylacetylene in 30 ml of THF. The mixture was then heated again at reflux for 30 min, and treated with dropwise addition of 5.172 g (25.11 mmoles) of 2-(phenylethynyl) benzaldehyde in 30 ml of THF. The final mixture was heated at reflux for 2 hr, cooled, treated with 1 liter of saturated ammonium chloride solution and extracted with 4 × 200 ml of ether. The ethereal extracts were combined, dried and concentrated to a yellow oil which was dissolved in 500 ml of carbon tetrachloride and concentrated. The excess phenylacetylene was removed by this treatment. The residual oil was then stirred with 300 ml of hexane. Upon standing overnight, the carbinol separated out as voluminous white flakes: yield, 3.50 g (11.6 mmoles, 46.3%); mp 73°C; IR (KBr) showed the expected OH absorption at 3600–3100 cm^{-1} and a weak 2210 cm^{-1} band; NMR ($CDCl_3$) δ 2.92 (broad d, 1H, OH), 6.20 (broad, d, 1H, methine), 7.16–8.16 ppm (m, 14H, aromatic).

The carbinol was dissolved in 200 ml of ether, cooled to 0°C and treated with 16 ml of a 0.67 M aqueous chromic acid solution. The dark brown mixture was stirred for 1.5 hr at 20°C and diluted with 200 ml of water. The aqueous phase was extracted with 2 × 200 ml of ether. The combined ethereal extracts were washed with 500 ml of saturated sodium bicarbonate solution and then with 3 × 200 ml of water. The ethereal solution now yellow was dried and concentrated. IR (neat) showed intense absorptions at 2200 and 1645 cm^{-1}, and the complete absence of the starting material. The oil was purified by silica gel column chromatography, eluting with 1 : 2 dichloromethane-hexane.

Thermal Intramolecular Cyclization Reaction of 1-(2-Phenylethynyl)phenyl-3-phenylpropynone. Synthesis of 10-Phenyl-11H-benzo[b]fluoren-11-one and its 5-Phenyl Isomer

1-(2-Phenylethynyl)phenyl-3-phenylpropynone obtained from the previous experiment was heated without a solvent at 150 ± 5°C under argon for 4 hr. The oil turned dark brown and solidified. Thin-layer chromatography on silica gel plate indicated complete disappearance of starting material. The crude solid was purified by silica gel column chromatography. The 1 : 2 dichloromethane-hexane eluant separated the major component. Removal of the solvent afforded orange yellow needles which were recrystallized from toluene to yield, in 2 crops, 1.754 g (5.732 mmoles, 49.4% overall from the carbinol); mp 217–218°C; IR (KBr) showed an intense peak at 1705 cm^{-1}; NMR ($CDCl_3$) δ 7.00–7.88 (m) and 7.92 (s), characteristic of 10-phenyl-11H-benzo[b]fluoren-11-one (Reference 176).

Anal. for $C_{23}H_{14}O$ (306.36):

Calculated: C, 90.17; H, 4.61.
Found: C, 90.22; H, 4.68.

The mother liquor after yielding the desired product was concentrated and recrystallized from ethanol. The yellow powdery solid had an NMR different from 10-phenyl-11H-benzo-[b]fluoren-11-one but matching that of the 5-phenyl isomer.

General Procedure for Polyisoimide Synthesis (TFAA method)

All glassware needed for the polymerization experiment were dried for several hours at 100°C. The monomers for the reaction, i.e., 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane-dianhydride (6FDA) and 4,4'-oxydianiline (ODA) were dried at 100°C/0.1 torr for 24 hours. The precise amount of 6FDA (6.441 g) was weighed out and transferred to a dried addition pouch. To a dried reaction vessel was placed 2.000 g of ODA and a magnetic stirring bar. The materials and glassware were dried at 100°C/0.1 torr for an additional 24 hours and were assembled while hot under argon. To the ODA powder was added 20 ml of anhydrous tetrahydrofuran (THF). At reflux, the solids dissolved completely and the 6FDA solid was added from the addition pouch in small portions. As the addition progressed, the solution became viscous. After complete addition and an additional 15 minutes, the viscous solution was diluted to 175 ml with anhydrous THF.

Under argon at 0°C, the solution was treated with dropwise addition of 3 ml of trifluoroacetor anhydride. The bulk solution immediately turned yellow. The solution was stirred at 0°C for 5 min then at 25°C for 2 hours, and then poured into 1 liter of saturated sodium bicarbonate to precipitate a yellow solid which was filtered, dried at 70°C/0.1 torr for 4 hours and reconstituted in 250 ml of fresh anhydrous THF. The yellow solution was poured into 1 liter of vigorously stirred hexane. The stringy yellow precipitate was filtered, pulverized under argon and dried at 90°C/0.1 torr for 8 hours.

General Synthesis of Poly (6FDA-ODA) isoimide in Tetrahydrofuran (DCC method)

6FDA was recrystallized twice from acetic anhydride and dried at 100°C/0.1 tor for 72 hr. ODA was sublimed twice at 180°C/0.005 torr.

Into a 125-ml addition pouch was placed 22.215g (50.034 mmoles) of 6FDA and into a 250-ml three-neck reaction vessel containing a stirbar was placed 10.000g (50.000 mmoles) of ODA. The glassware and reactants were dried at 100°C/0.1 torr for 16 hr. and assembled under argon while hot. The assembly was cooled to 25°C. Into the reaction vessel was

introduced 150 ml of freshly distilled (from calcium hydride) tetrahydrofuran (THF). Brief warming of the slurry facilitated solubilization of the ODA particles in THF. The pale yellow solution was treated with the powdered 6FDA added in small portions from the addition pouch. After each partial addition, the mixture was vigorously stirred until all particles dissolved before adding a new portion. A slight exotherm was detected as the reaction progressed. The complete addition required 45 min. The viscosity of the light yellow solution rose markedly. Toward the end of the addition, stirring was no longer possible. The viscous solution was moved around over the interior surface area in order to pick up the trace quantity of powder adhering to the glass surface. The transparent viscous solution (21.48% solid content was warmed at 60°C for 30 min and cooled to 25°C.

To a 3-liter three-neck flask equipped with a mechanical stirrer and a gas inlet fitting for argon was added 500 ml of freshly distilled THF. The viscous polymer solution (almost like a gel) was transferred in with the aid of a spatula. Upon stirring the pieces of the gel slowly enter into solution. The small amount of the viscous polymer solution still adhered to the reaction vessel was diluted with 50 ml of anhydrous THF and slowly added (with a pipette) to a 500 ml volume of vigorously stirred hexane. White strings of polymer readily formed. They were dried under a slow stream of argon. Yield, 3.313g.

A small batch of this white stringy polymer was further dried at 100°C/0.1 torr for 24 hr before viscosity measurement. The inherent viscosity was determined to be 1.35 (THF, 30.0°C).

The 3-liter reaction flask containing the 500-ml THF solution of the polymer (28.902g) was treated with another 700 ml of THF and then with 12.005g (58.277 mmoles) of N,N'-dicyclohexylcarbodiimide (DCC) which was added dropwise as a 100-ml THF solution. After 10 ml of the DCC solution was added, the bright yellow solution turned into a gelatinous mass. More THF was added to dissolve the gel. A total final volume of 2 liters was attained. The rest of the DCC solution was then added over 5 min. Dicyclohexylurea began to precipitate and the mixture was stirred at 25°C under argon for 24 hr. Another portion of DCC (12.002g) was added and stirring was continued at 25°C for another 24 hrs.

The white solid was filterd using a porcelain Büchner funnel and Whatman Number 3 Filter paper, and rinsed with anhydrous THF. The bright yellow filtrate was concentrated to 500 ml and slowly poured into 2.5 liters of vigourously stirred hexane. Long strings of the bright yellow polyisoimide polymer were obtained and dried thoroughly.

The crude polymer was reconstituted in 300 ml of anhydrous THF under argon. The solution was transferred to an addition funnel and added dropwise but rapidly to a vigorously stirred 1-liter volume of hexane. The precipitated polymer was isolated and dried at 90°C/0.1 torr for 2 days.

Differential Scanning Calorimetry (DSC) of high molecular weight polyisoimides in general exhibit a mild and broad exotherm maximizing at 290°C.

Purification of N-Isopropyl-2-pyrrolidinone

A 1-liter quantity of crude N-isopropyl-2-pyrrolidinone (GAF Corporation) was mixed with 200 ml of benzene and the mixture was heated to effect azeotropic distillation of water. At the end of the distillation period, the condensate around the condenser cold finger appeared clear. The benzene was then distilled off. As the temperature of the condensate at the distilling head rose to 120°C, the distillation was terminated and the distilling flask was cooled prior to a second distillation under reduced pressure. Approximately 800 ml of distillate was collected at 95–98°C/10 torr and stored under argon in a brown bottle until use.

Synthesis of Poly(6FDA-ODA) isoimide in N-Isopropyl-2-pyrrolidinone (DCC method)

6FDA was recrystallized three times from acetic anhydride and dried for 48–72 hr. at 100°C/0.1 torr. 4,4'-Oxydianiline was sublimed twice at ca. 180°C/0.55 torr and was obtained as a crystalline and lustrous white solid. Both monomers were kept under argon inside a desiccator until use.

6FDA (22.215g, 50.035 mmoles) was weighed out and transferred to a 125-ml addition pouch. ODA (10.005g, 50.025 mmoles) was weighed out and placed inside a 250-ml three-necked reaction vessel containing a magnetic stirbar. All glassware and materials were further dried at 100°C/0.1 torr for 60 hr and assembled under argon while hot. The assembly was cooled to 25°C. Into the reaction vessel was introduced exactly 120 ml of freshly distilled N-isopropyl-2-pyrrolidone (NIP). ODA entered in solution upon stirring at 25°C for 15 min, giving a yellow orange solution. 6FDA was then added to the solution by the pinchful. The mixture was warmed to 70–75°C using a water bath as the external souce, so that the added 6FDA entered in solution more readily. After each partial addition, the mixture was vigorously stirred until all particles dissolved before adding a new portion. It was evident that the viscosity of the orange brown solution rose markedly. Toward the end of the addition (1 hr), the stirring was difficult even at 70–75°C. The viscous solution was moved around over the interior surface area in order to pick up the trace quantity of powder adhering to the glass surface. The transparent viscous solution 26.85% solid content was stirred and warmed at 70–75°C for an additional 2 hr. To prepare a solution for viscosity measurement, a 0.8-ml aliquot of this solution was transferred to a 25-ml volumetric flask and diluted to the mark with NIP.

To a 3-liter three-neck flask equipped with a mechanical stirrer and a gas-inlet fitting for argon was added 500 ml of tetrahydrofuran (freshly distilled from calcium hydride). The viscous polymer solution was then allowed to drip in. Stirring effected thorough mixing. The small amount of the viscous solution still adhered to the flask was diluted with 50 ml of anhydrous THF and poured slowly into 400 ml of anhydrous dichloromethane. The turbid mixture was further treated with 400 ml of Spectroquality hexane to precipitate a white solid which was isolated by filtration and drying under a slow stream of argon.

A small batch of this white powdery solid was further dried at 100°C/0.1 torr for 4 hr before viscosity measurement. The inherent viscosity measured in NIP and at 30.0°C was 0.33.

The 3-liter reaction flask containing the 500-ml THF solution of the polymer was treated with 12.081g (58.646 mmoles) of N,N'-dicyclohexylcarbodiimide (DCC). The volume of the final mixture was made up to 1500 ml with anhydrous THF. After stirring at 25°C for 15 min., the solution became turbid and dicyclohexylurea (DCU) began to precipitate. The mixture was stirred at 25°C under argon for 24 hr, treated with a fresh portion (12.215g, 59.296 mmoles) of DCC, stirred for another 40 hr, and filtered to remove DCU.

The filtrate was concentrated to 500 ml final volume, diluted with 500 ml of dichloromethane, and poured into 1.5 liters of vigorously stirred hexane. The stringy yellow precipitate was filtered, pulverized under argon and dried at 90°C/0.1 torr for 24 hr.

SECTION IV

CONCLUSIONS

A variety of novel methods for an efficient synthesis of the IMC curable monomer, 2,2′-bis (phenylethynyl)-4,4′,5,5′-tetraaminobiphenyl, was explored without success. A convenient organolithium route was found for the preparation of another IMC curable monomer, 2,2′-bis(phenylethynyl)-5,5′-diaminobiphenyl. During the synthetic study, it was further established that palladium-catalyzed phenylethynylation of 2,2′-dihalo-5,5′-dinitrobiphenyl did not yield the expected 2,2′-bis(phenylethynyl)-5,5′-dinitrobiphenyl. The palladium catalysis approach in synthesis is attractive but should be applied with discretion.

A few categories of model compounds with potential IMC reactions were prepared and characterized by thermal analysis. Reaction parameters for the synthesis of high molecular weight polyisoimides were studied. The isoimide polymers synthesized were used for study of the thermal isoimide-to-imide rearrangement as an IMC-type reaction.

REFERENCES

1. H.F. Mark, Macromolecules, 10, 881 (1977).
2. F.L. Hedberg and F.E. Arnold, Technical Report, AFML-TR-74-278, June, 1975.
3. P.M. Hergenrother, Preprints, Amer. Chem. Soc., Div. Org. Coatings and Plastics, 35, 166 (1975).
4. A.L. Landis, N. Bilow, R.H. Boschan, R.E. Lawrence, and T.J. Aponyi, Preprints, Amer. Chem. Soc., Div. Polym. Chem., 15, 537 (1974).
5. N. Bilow, A.L. Landis, and T.J. Aponyi, Soc. Adv. Mat. Process Eng., Series 20, 618 (1975).
6. R.F. Kovar, G.F.L. Ehlers, and F.E. Arnold, Technical Report, AFML-TR-76-71, June, 1976.
7. R.F. Kovar, G.F.L. Ehlers, and F.E. Arnold, J. Polym. Sci., Polym. Chem Ed., 15, 1081 (1977).
8. W. Jarre, D. Bieniek and F. Korte, Naturwissenschaften, 62. 391 (1975).
9. J.M. Pickard, S.C. Chattoraj, G.A. Loughran, and M.T. Ryan, Macromolecules, 13, 1289 (1980).
10. R.F. Kovar, G.F.L. Ehlers, and F.E. Arnold, Technical Report, AFML-TR-76-28, June, 1976.
11. S.A. Kandil and R.E. Dessey, J. Amer. Chem. Soc., 88, 3027 (1966).
12. E.H. White and A.A.F. Sieber, Tetrahedron Lett., 2713 (1967).
13. F.L. Hedberg and F.E. Arnold, Preprints, Amer. Chem. Soc., Div. Polym. Chem., 16, 677 (1975).
14. F.L. Hedberg and F.E. Arnold, J. Polym. Sci., Polym. Chem. Ed., 14, 2607 (1976).
15. F.L. Hedberg and F.E. Arnold, Technical Report, AFML-TR-76-198, [illegible] h, 1977.
16. F.E. Arnold, U.S. Pat. Appl. 678, 324; 19 April 1976; Chem. Abst., 86, 73797a (1977); U.S. Pat. Appl. 678, 325; 19 April 1976; Chem. Abst., 86, 90587z (1977).
17. A. Banihashemi and C.S. Marvel, J. Polym. Sci., Polym. Chem. Ed., 15, 2653 (1977); ibid, 15, 2667 (1977).

18. R.L. Frentzel and C.S. Marvel, J. Polym. Sci., Polym. Chem. Ed., 17, 1073 (1979).
19. V. Sankaran, S.C. Lin, and C.S. Marvel, J. Polym. Sci., Polym. Chem. Ed., 18, 495 (1980).
20. A. Somers and C.S. Marvel, J. Polym. Sci., Polym. Chem. Ed., 18, 1511 (1980).
21. P.Y. Chen and C.S. Marvel, J. Polym. Sci., Polym. Chem. Ed., 19, 619 (1981).
22. F.L. Hedberg, P.M. Lindley, C.Y-C. Lee, and I.J. Goldfarb, J. Polym. Sci, Polym. Chem. Ed., 20, 3069 (1982).
23. B.A. Reinhardt and F.E. Arnold, Technical Report, AFML-TR-78-141, December 1978; Preprints, Amer. Chem. Soc., Div. Polym. Chem., 20, 211 (1979).
24. K. Lauer, J. prakt. Chem., 137, 175 (1933).
25. H.A. Dieck and R.F. Heck, J. Organometal. Chem., 93, 259 (1975).
26. Y. Tohda, K. Songashira, and N. Hagihara, Synthesis, 777 (1977).
27. E.T. Sabourin, Preprints, Amer. Chem. Soc., Div. Petrol. Chem., 233 (1979).
28. R.D. Stephens and C.E. Castro, J. Org. Chem., 28, 3313 (1963).
29. M.S. Shvartsberg, I.L. Kotlyarevskii, A.N. Kozhevnikova, and V.N. Andrievskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1144 (1970).
30. M.S. Shvartsberg, L.N. Bizhan, and I.L. Kotlyarevskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1534 (1971).
31. P.E. Fanta, Synthesis, 9 (1974); Chem. Rev., 64, 613 (1964); Chem. Rev., 38, 139 (1946).
32. M. Goshaev, O.S. Otroshchenko, and A.S. Sadykov, Russ. Chem. Rev. (English Translation), 41, 1046 (1972).
33. G. Gaekwad and S. Sethna, J. Indian Chem. Soc., 55, 794 (1978).
34. P.J. Wittek, T.K. Liao, and C.C. Cheng, J. Org. Chem., 44, 870 (1979).
35. S. Gronowitz and K. Dahlgren, Ark. Kemi, 21, 201 (1963).
36. R.C. Fuson and E.A. Cleveland, Org. Synth. Coll. Vol. III, 339 (1955).
37. R.D. Rieke and L.D. Rhyne, J. Org. Chem., 44, 3445 (1979).
38. S. Miyano, M. Tobita, M. Nawa, S. Sato, and H. Hashimoto, J. Chem. Soc. Chem. Comm., 1233 (1980).
39. J. Cornforth, A.F. Sierakowski, and T.W. Wallace, J. Chem. Soc. Chem. Commun., 294 (1979).
40. M.S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances", Prentice-Hall, Englewood Cliffs, N.J., 1954, Chapter V.
41. W.B. Smith, J. Org. Chem., 26, 4206 (1961).
42. J.P. Morizur and R. Pallaud, C.R. Acad. Sci., 252, 3074 (1961).

43. A. McKillop, L.F. Elsom, and E.C. Taylor, Tetrahedron, 26, 4041 (1970); Org. Syn., 55, 48 (1976); J. Amer. Chem. Soc., 90, 2423 (1968).

44. J.P. Morizur, Bull. Soc. Chim. France, 1331 (1964).

45. R.L. Clough, P. Mison, and J.D. Roberts, J. Org. Chem., 41, 2252 (1976).

46. S.K. Taylor, S.G. Bennett, K.J. Heinz, and L.K. Lashley, J. Org. Chem., 46, 2194 (1981).

47. R. Pallaud and J.M. Pleau, C.R. Acad. Sci., Ser. C, 267, 507 (1968).

48. B. Sarry and W. Hanke, Z. Anorg. Allg. Chem., 286, 229 (1958).

49. E. Wenkert, T.W. Ferreira, and E.L. Michelotti, J. Chem. Soc. Chem. Commun., 637 (1979).

50. S.I. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita, and K. Kondo, J. Org. Chem., 44, 2408 (1979).

51. A.S. Kende and D.P. Curran, Tetrahedron Lett., 3003 (1978).

52. S.W. Breuer and F.A. Broster, Tetrahedron Lett., 2193 (1972).

53. M.F. Semmelhack, P.M. Helquist, and L.D. Jones, J. Amer. Chem. Soc, 93, 5908 (1971).

54. M.F. Semmelhack and L.S. Ryono, J. Amer. Chem. Soc., 97, 3873 (1975).

55. A.S. Kende, L.S. Liebeskind, and D.M. Braitsch, Tetrahedron Lett., 3375 (1975).

56. M. Mori, Y. Hashimoto, and Y. Ban, Tetrahedron Lett., 631 (1980).

57. M. Zembayashi, K. Tamao, J. Yoshida, and M. Kumada, Tetrahedron Lett., 4089 (1977).

58. K. Takagi, N. Hayama, and S. Inokawa, Chem. Lett., 917 (1979).

59. P. Bamfield and P.M. Quan, Synthesis, 537 (1978).

60. L.G. Makarova and A.N. Nesmeyanov, "The Organic Compounds of Mercury", Methods of Elemento-Organic Chemistry Series, Volume 4, A.N. Nesmeyanov, K.A. Kocheshkov, editors, North-Holland Publishing Company, Amsterdam, 1967.

61. L.G. Makarova in Organometallic Reactions, Vol. 1, E.I. Becker and M. Tsutsui, ed., Wiley, New York, N.Y., 1970, pp. 271-274; ibid., Vol. 2, 1971, pp. 414-417.

62. R.F. Heck, J. Am. Chem. Soc., 90, 5535, 5546 (1968).

63. M.O. Unger and R.A. Fouty, J. Org. Chem., 34, 18 (1969).

64. A. Kasahara, T. Izumi, M. Yodono, R. Saito, T. Takeda, and T. Sugawara, Bull. Chem. Soc. Japan, 46, 1220 (1973).

65. T. Izumi, T. Iino, and A. Kasahara, Bull. Chem. Soc. Japan, 46, 2251 (1973).

66. R.A. Kretchmer and R. Glowinski, J. Org. Chem., 41, 2661 (1976).

67. R.C. Larock and J.C. Bernhardt, J. Org. Chem., 42, 1680 (1977).

68. J. Bergman, Tetrahedron, 28, 3323 (1972).

69. S. Uemura, M. Wakasugi, and M. Okano, J. Org. Chem., 45, 277 (1980).

70. A. McKillop, A.G. Turrell, and E.C. Taylor, J. Org. Chem., 42, 764 (1977).

71. E.C. Taylor and A. McKillop, Accts. Chem. Res., 3, 338 (1970).

72. A. McKillop and E.C. Taylor, Adv. Organometal. Chem., 11, 147 (1973).

73. A. McKillop, Pure Appl. Chem., 43, 463 (1975).

74. A. McKillop and E.C. Taylor, Endeavor, 35, 88 (1976).

75. A. McKillop, J.D. Hunt, M.J. Zelesko, J.S. Fowler, E.C. Taylor, G. McGillivray and F. Kienzle, J. Amer. Chem. Soc., 93, 4841 (1971).

76. E.C. Taylor, H.W. Altland, and A. McKillop, J. Org. Chem., 40, 3441 (1975).

77. E.C. Taylor, E.C. Bigham, D.K. Johnson, and A. McKillop, J. Org. Chem., 42, 362 (1977).

78. E.C. Taylor, H.W. Altland, R.H. Danforth, G. McGillivray, and A. McKillop, J. Amer. Chem. Soc., 92, 3520 (1970).

79. A. McKillop, B.P. Swann, M.J. Zelesko, and E.C. Taylor, Angew. Chem. Internat. Ed. Engl., 9, 74 (1970).

80. A. McKillop, J.S. Fowler, M.J. Zelesko, J.D. Hunt, E.C. Taylor, and G. McGillivray, Tetrahedron Lett., 2423 (1969).

81. E.C. Taylor, J.G. Andrade, and A. McKillop, J. Chem. Soc. Chem. Commun., 538 (1977).

82. E.C. Taylor, J.G. Andrade, G.J.H. Rall, and A. McKillop, Tetrahedron Lett., 3623 (1978).

83. E.C. Taylor, J.G. Andrade, G.J.H. Rall, and A. McKillop, J. Org. Chem., 43, 3632 (1978).

84. V.V. Lapin and D.V. Tishchenko, Zh. Prikl. Khim., 45, 923 (1972); English Edition, 45, 960 (1972).

85. A. Bistrzycki and F. Ulffers, Ber., 23, 1876 (1890).

86. K.S.Y. Lau and D.I. Basiulis, Tetrahedron Lett., 1175 (1981).

87. A novel TTFA-promoted oxidative intramolecular cyclization of alicyclic dicarboxylic acids has been reported recently: E.C. Taylor, G.E. Jagdmann, Jr., and A. McKillop, J. Org. Chem., 45, 3373 (1980).

88. M.S. Kharash, F.W.M. Lommen and I.M. Jacobsohn, J. Amer. Chem. Soc., 44, 793 (1922).

89. S.S. Guha-Sircar and M.K. Rout, J. Indian Chem., 29, 779 (1952).

90. H. Gilman and B.J. Gaj, J. Org. Chem., 22, 447 (1957).

91. M.S. Newman and H. Boden, Org. Synth. Coll. Vol. V, 1029 (1973).

92. W. Baker, J.R.W. McOmie, D.R. Preston, and V. Rogers, J. Chem. Soc., 414 (1960).

93. R. Rothuis, J.J.H.M. Font Freide, and H.M. Buck, Recueil trav. chim. Pays-Bas, 92, 1308 (1973).

94. K. Sonagashira, Y. Tohda, and N. Hagihara, Tetrahedron Lett., 4467 (1975).

95. L. Cassar, J. Organometal. Chem., 93, 253 (1975).

96. K. Ishizu, U.D.G. Prabhu, D. Draney, B.H. Lee, and C.S. Marvel, J. Polym. Sci., Polym. Chem. Ed., 20, 2851 (1982).

97. H. Yamanaka, M. Shiraiwa, K. Edo, and T. Sakamoto, Chem. Pharm. Bull, 27, 270 (1979).

98. K. Edo, H. Yamanaka, and T. Sakamoto, Heterocycles, 9, 271 (1978).

99. R.E. Atkinson, R.F. Curtis, D.M. Jones, and J.A. Taylor, J. Chem. Soc. C., 2173 (1969).

100. H.G. Viehe and V. Jäger, "Methoden der Organischen Chemie (Houben-Weyl)", Vol. V/2a, E. Müller, ed., George Thieme Verlag, Stuttgart, 1977.

101. R.F. Heck, Accts. Chem. Res., 12, 146 (1979).

102. F.L. Hedberg and M.R. Unroe, Technical Report, AFWAL-TR-81-4156, November 1981.

103. Compound 38 was synthesized using commercially available 9-bromophenanthrene (Aldrich) as starting material. A lithiation-iodination sequence yielded 9-iodophenanthrene (70% yield) which underwent palladium-catalyzed phenylethynylation to give 38. 9-Iodophenanthrene was previously obtained in 45% yield from its amino precursor (M.A. Goldberg, E.P. Ordas, and G. Carsch, J. Amer. Chem Soc., 69, 260 (1947).)

104. Compound 39a was previously prepared through a ring opening-homologation reaction of a dichlorocarbene adduct (E. Wada, S. Fujisaki, A. Nakashima, and S. Kajigaeshi, Bull. Chem. Soc. Japan, 48, 739 (1975).) We synthesized compound 39a via the Wittig reaction of the more readily available fluorenone and (3-phenyl-1,2-propadienyl)triphenylphosphonium bromide (H. Saikachi, N. Shimojyo, and H. Ogawa, Yakugaku Zasshi, 90, 581 (1970); Chem. Abstr., 73, 35456 n (1970).)

105. M. Rabinovitz, I. Agranat, and E.D. Bergmann, J. Chem. Soc., (B), 1281 (1967).

106. W.B. Austin, N. Bilow, W.J. Kelleghan, and K.S.Y. Lau, J. Org. Chem., 46, 2280 (1981).

107. Addition of arylpalladium across double bonds and triple bonds is well known. See: H.A. Dieck and R.F. Heck, J. Amer. Chem. Soc., 96, 1133 (1974); K. Kaneda, T. Uchiyama, Y. Fujiwara, T. Imanaka, and S. Teranishi, J. Org. Chem., 44, 55 (1979).

108. D. Coulson, Inorganic Synthesis, 12, 112 (1972).

109. G.A. Olah and S.J. Kuhn, Org. Synth. Coll. Vol. V, 480 (1973); J. Amer. Chem. Soc., 83, 4564 (1961).

110. B.F. Aunsley, G. Hetherington, and P.L. Robinson, J. Chem. Soc., 1119 (1954).

111. G.A. Olah, S.J. Kuhn, and S.H. Flood, J. Amer. Chem. Soc., 83, 4571, 4581 (1961).

112. L.M. Yagupolskii, I.I. Maletina and V.V. Orda, J. Org. Chem. USSR, 10, 2240 (1974).

113. M. Schmeisser, P. Sartori, and B. Lippsmeier, Z. Naturforsch., 28-B, 573 (1973).

114. S.K. Yarbro, R.E. Noetle and W.B. Fox, J. Fluorine Chem., 6, 187 (1975).

115. F. Effenberger and J. Geke, Synthesis, 40 (1975).

116. H. Schultheiss and E. Fluck, Z. Anorg. Allg. Chem., 286, 20 (1978).

117. C.L. Coon, W.G. Bluchner, and M.E. Hill, J. Org. Chem., 38, 4243 (1973).

118. A. Onopchenko, E.T. Sabourin, and C.M. Selwitz, J. Org. Chem., 44, 1233 (1979).

119. W. Ried, N. Kothe, R. Schweitzer, and A. Höhle, Chem. Ber., 109, 2921 (1976).

120. W. Ried and R. Schweitzer, Chem. Ber., 109, 1643 (1976).

121. E.R.H. Jones and F.G. Mann, J. Chem. Soc., 786 (1950).

122. A.C. Hontz and E.C. Wagner, Org. Syn. Coll. Vol. IV, 383 (1963).

123. K.S.Y. Lau and F.E. Arnold, Technical Report, AFWAL-TR-79-4065, May 1979.

124. W. Münzenmaier and H. Straub, Synthesis, 49 (1976).

125. G. Favini and J.R. Bellobono, Gazz. Chem. Ital., 96, 1423 (1966).

126. A.H.A. Tinnemans and W.H. Laarhoven, J. Chem. Soc., Perkin Trans II, 1104, 1111, 1115 (1976).

127. H. Gilman, S.G. Cottis, and W.H. Atwell, J. Amer. Chem. Soc., 86, 1596 (1964).

128. E.H. Braye, W. Hübel and I. Caplier, J. Amer. Chem. Soc., 83, 4406 (1961).

129. S.Y. Delavarenne and H.G. Viehe, Chemistry of Acetylenes, H.G. Viehe, Ed., Marcel Dekker, Inc., publisher, New York, NY, Chapter 10, 1969, pp. 651ff.

130. J.K. Stille and K.S.Y. Lau, Accts. Chem. Res., 10, 434 (1977).

131. J. Ficini and C. Barbara, Bull. Soc. Chim. France, 2787 (1965).

132. T. Curtius and K. Thun, J. präkt. Chem., 44, 161 (1891).

133. W.T. Flowers, D.R. Taylor, A.E. Tipping, and C.N. Wright, J. Chem. Soc. (C), 1986 (1971).

134. K. Issleib and A. Balszuweit, Chem. Ber., 99, 1316 (1966).

135. M.E. Landis and J.C. Mitchell, J. Org. Chem., 44, 2288 (1979).

136. H.H. Hatt, Org. Synth. Coll. Vol. II, 208 (1943).

137. M. Farnier, S. Soth, and P. Fournari, Can. J. Chem., 54, 1083 (1976).

138. R.D. Stephens and C.E. Castro, J. Amer. Chem. Soc., 86, 4358 (1964).

139. T. Abraham, J. Polym. Sci., Polym. Chem. Ed., 20, 1953 (1982).

140. H.F. Ridley, R.G.W. Spickett, and G.M. Timmis, J. Heterocyclic Chem., 2, 453 (1965).

141. R.B. Woodward and R. Hoffmann, Angew. Chem. Internat. Ed. Engl., 8, 781 (1969).

142. W. Oppolzer, Angew. Chem. Internat. Ed. Engl., 16, 10 (1977).

143. G. Brieger and J.N. Bennett, Chem. Rev., 80, 63 (1980).

144. T. Kametani and H. Nemoto, Tetrahedron, 37, 3 (1981).

145. I.L. Klundt, Chem. Rev., 70, 471 (1970).

146. R.L. Funk and K.P.C. Vollhardt, Chem. Soc. Rev., 9, 41 (1980).

147. W. Oppolzer and K. Keller, J. Amer. Chem. Soc., 93, 3836 (1971).

148. T. Kametani, H. Nemoto, H. Ishikawa, K. Shirogama, H. Matsumoto, and K. Fukumoto, J. Amer. Chem. Soc., 99, 3461 (1977).

149. H.F. Schmitthenner and S.M. Weinreb, J. Org. Chem., 45, 3373 (1980).

150. J.G. Cannon, T. Lee, F.L. Hsu, J.P. Long, and J.R. Flynn, J. Med. Chem., 23, 502 (1980).

151. W. Oppolzer, E. Francotte, and K. Battig, Helv. Chim. Acta, 64, 478 (1981).

152. O.L. Chapman, M.R. Engel, J.P. Springer, and J.C. Clardy, J. Amer. Chem. Soc., 93, 6696 (1971).

153. M.P. Cava and D.P. Napier, J. Amer. Chem. Soc., 79, 1701 (1957); ibid, 80, 2255 (1958).

154. A.T. Bloomquist and V.J. Hruby, J. Amer. Chem. Soc., 89, 4996 (1967).

155. A. Sanders and W.P. Giering, J. Org. Chem. Soc., 38, 3055 (1973).

156. H.H. Wasserman and J. Soladar, J. Amer. Chem. Soc., 87, 4002 (1965).

157. F.M. Logullo, A.H. Seitz, and L. Friedman, Org. Syn. Coll. Vol. V, 54 (1973).

158. W.A. Bubb and S. Sternhell, Aust. J. Chem., 29, 1685 (1976).

159. B.J. Arnold, P.G. Sammes, and T.W. Wallace, Perkin Trans I, 415 (1974).

160. T. Kutsuma, I. Nagayama, T. Okazaki, T. Sakamoto, and S. Akaboshi, Heterocycles, 8, 397 (1977).

161. K.L. Dhawan, B.D. Gowland, and T. Durst, J. Org. Chem., 45, 922 (1980).

162. E. Akgun, M.B. Glinski, K.K. Khawan, and T. Burst, J. Org. Chem., 46, 2730 (1981).

163. M.P. Cava and K. Muth, J. Amer. Chem. Soc., 82, 652 (1960).

164. H.C. Brown, C.P. Garg, and K.T. Liu, J. Org. Chem., 36, 387 (1971).

165. C.E. Castro, E.J. Gaughan, and D.C. Owsley, J. Org. Chem., 31, 4071 (1966).

166. H. Saikachi, N. Shimojyo, and H. Ogawa, Yakugaku Zasshi, 90, 581 (1970); Chem. Abst., 73, 35456n (1970).

167. W. Kirmse and K. Muth, Chem. Ber., 91, 000 (1958).

168. J.A. Skorcz and J.E. Robertson, J. Med. Chem., 6, 255 (1965).

169. K.S.Y. Lau, P.K. Wong, and J.K. Stille, J. Amer. Chem. Soc., 98, 5832 (1976).

170. E. Müller, C. Beißner, H. Jäckle, E. Langer, M. Muhm, G. Odenigbo, M. Sauerbier, A. Segnitz, A. Streichfuß, and R. Thomas, Liebigs Ann. Chem., 754, 64 (1971).

171. E. Müller, W. Münzenmaier, and H. Straub, Chem.-Ztg., 97, 446 (1973).

172. F. Wagner and H. Meier, Tetrahedron, 30, 773 (1974).

173. H.A. Staab and B. Draeger, Chem. Ber., 105, 2320 (1972).

174. E. Müller and W. Winter, Liebigs Ann. Chem., 1876 (1974).

175. E. Müller and C. Beißner, Chem.-Ztg., 97, 207 (1973).

176. W. Ried and G. Clauß, Liebigs Ann. Chem., 953 (1975).

177. E. Müller and G. Zountas, Chem.-Ztg., 98, 41 (1974).

178. W. Winter, Angew. Chem. Internat. Ed. Engl., 14, 170 (1975).

179. E. Müller and G. Zountas, Chem.-Ztg., 97, 446 (1973).

180. W. Winter, Tetrahedron Lett., 3913 (1975).

181. A.L. Landis, Final Report, for Contract AFWAL F33615-82-C-5016 "Chemistry for Processible Acetylene-Terminated Imides", July, 1983.

182. J.A. Kreuz, "Copolyimide-Isoimide Polymers", U.S. Patent 3,413,267; issued November 26, 1968.

183. M. Roth, "Process for the Manufacture of Isoimides or Mixtures of Isoimides and Imides", U.S. Patent 4,179,444; issued December 18, 1979.

184. W.I. Awad, A.S. Wasfi, and M.J.S. Ewad, J. Iraqi Chem. Soc., 2, 5 (1977).

185. J. Zurakowska-Orsz'agh, A. Orzeszko, and T. Chreptowicz, European Polym. J., 16, 289 (1979).

186. C.E. Sroog, Macromol. Synth., Coll. Vol. I, 295 (1970).

187. P. Hubert and O.G. Vitzthum, Angew. Chem. Internat. Ed. Engl., 17, 710 (1978).

188. G. Wilke, Angew. Chem. Internat. Ed. Engl., 17, 701 (1978).

189. K. Zosel, Angew. Chem. Internat. Ed. Engl., 17, 702 (1978).

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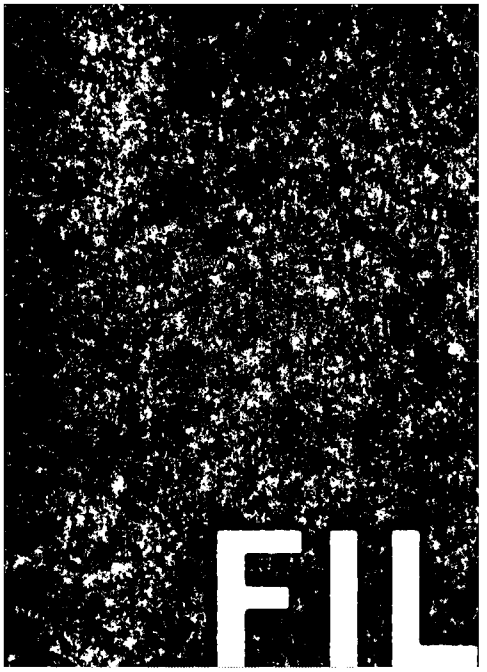
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